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FATE OF DDT AND NITRATE IN GROUND WATER

Marion R. Scalf, et al

Robert S. Kerr Water Research Center
Ada, Oklahoma

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FATE OF DDT AND NITRATE IN GROUND WATER

by

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PREFACE

The intelligent management of water resources in the United States is necessarily based on considerations of both quantity and quality.

An attractive possibility for the conservation of areal water exists in the Southern High Plains of northwestern Texas and eastern New Mexico where surface runoff is collected in natural basins called playas. To prevent extensive losses by evaporation, this runoff water could be injected into the Ogallala Aquifer, the area's major water supply.

Although most of the ground water pumped in this area is used for irrigation of agricultural lands, many cities and towns and thousands of farmers also pump water from the same aquifer for household use. The water supply available for recharge is mostly runoff water from agricultural lands and may contain chemicals harmful to man or animals. There is justifiable concern over the safety of drinking water supplies exposed to these chemicals and other pollutants. However, there is a notable lack of reliable data and facts concerning the movement, degradation, and disappearance of toxic materials which are used on watersheds and may enter ground waters by ground-water recharge. This report is intended to illuminate part of the darkness now surrounding the subject.

This project was unique from a standpoint other than its concern with ground-water quality and the corresponding hydraulics of recharge operations--the United States Departments of the Interior and of Agriculture combined their diverse facilities and human competencies.

Under formal agreement, personnel of the Robert S. Kerr Water Research Center, U. S. Department of the Interior, and of the Southwestern Great Plains Research Center, U. S. Department of Agriculture, worked together on field and laboratory phases of this project as well as report preparation.

This cooperation paid off in a number of ways. The area of research was of mutual concern and, since each agency contributed certain facilities and services that were not readily available to the other, the project moved with greater efficiency, at reduced cost, and produced highly satisfactory results. This union of resources demonstrated the research economy and professional compatibility needed in practical resources conservation and management.

PROJECT DESCRIPTION

The objectives of this project were as follows:

1. To determine the distance and manner in which DDT and nitrate move from a well that is being recharged;

2. To determine the degree to which the aquifer will adsorb DDT and nitrate;

3. To study the manner in which DDT and nitrate are released from an aquifer by pumping a well which has been recharged for a specified time with water containing measured concentrations of these substances; and

4. To perform these tests under conditions where recharge rates, discharge rates, water-level fluctuations, and the physical and hydraulic characteristics of the aquifer are described and recorded sufficiently so as to extend results of this project to other ground-water situations.

The field facilities of the Southwestern Great Plains Research Center at Bushland, Texas were selected as the site for conduct of this project. This site offered the following conditions and advantages:

1. It contained a large-capacity well that could be used for recharging the Ogallala Formation and could also be pumped at high rates.

2. There were several very well constructed observation wells at varying distances from the recharge well where water samples could be collected during the test. Only one additional observation well was considered to be needed.

3. An irrigation well capable of providing adequate water for the recharge phase was present. This well was far enough from the recharge well that the influence of its pumping would not affect conditions resulting from recharge operations.

4. Thorough and accurate geologic and hydraulic information on the aquifer had already been obtained by personnel at the Southwestern Great Plains Research Center.

5. Aquifer conditions at this site were believed to be fairly representative of many of the heavily pumped areas of the Ogallala, particularly of those where playa water is available for recharge.

6. The point at which recharge water would enter the receiving formation was so far removed from any domestic or stock wells and so distant from any privately-owned lands that the tests would pose no pollutional hazards.

ACKNOWLEDGEMENTS

In projects of this nature, it is important that a full measure of appreciation be extended to those who contributed significantly to the project's successful completion.

These people are:

From the Robert S. Kerr Water Research Center:

Bert E. Bledsoe, Chemist
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Bobby D. Newport, Physical Science Technician
Tommy N. Redman, Engineering Aid

From the Southwestern Great Plains Research Center:

Ordie R. Jones, Hydraulic Engineering Technician
Oliver R. Lehman, Agricultural Research Technician
Donald C. Signor, Agricultural Engineer
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I. INTRODUCTION

General Extent and Cause of Problem

Increasing demands on the water resources of the High Plains area of West Texas and Eastern New Mexico have given rise to the very real possibility of storing water underground. This would be accomplished by recharging the Ogallala Aquifer--the area's major source of water. Water storage in aquifers is highly desirable because large storage volumes are available, water is available wherever the aquifer exists, little or no water is lost from aquifers by evaporation, ground-water quality is usually good, ground waters are not easily polluted, and often there is no other feasible storage site.

Artificial recharge practices give rise to concern that ground water may be contaminated by undesirable substances introduced with the recharge water.

Pesticides and nitrates are of particular importance in future recharge programs because of their association with agricultural practices in the High Plains area.

This report presents findings concerned with the fate of DDT and nitrate under actual recharge conditions in the Ogallala Aquifer.

DDT in Ground Water

The extent of ground-water pollution with pesticides is not known at this time; however, they are used in every section of the country

and, hence, are potential pollutants in all states. Artificial recharge is carried out to some extent in all sections of the country and as water use increases will become more important and widespread, creating increased opportunity for pollution of ground water.

The movement of pesticides through an aquifer from a recharge well and the concentration of these compounds in water subsequently pumped from the aquifer will obviously be greatly affected by the degree of adsorption of the pesticides by aquifer solids. The adsorption of pesticides on aquifer particles is a complex phenomenon involving many variables. Little work has been done concerning pesticide adsorption and saturated ground-water flow in aquifers, but there is considerable literature dealing with the behavior of pesticides in soils and surface waters.[1,2,3,4,5]

Extrapolation of soil research to aquifers indicates that the mineral composition of particles constituting an aquifer will strongly affect adsorption. Increasing proportions of clays, particularly the montmorillionites, would be expected to result in greater adsorption because of the ionic nature and large surface areas of these substances. Aquifers generally, however, have a low clay content and high percentages of sand or coarser material likely to be of lesser adsorptive capacity. Amorphous and crystalline hydroxides and oxides of aluminum, iron, and silica, which have large surface areas, would likewise be expected to increase adsorption capacities of aquifer particles. Such compounds

are present in minor, but possibly important, amounts in the aquifer material of the Ogallala. Also, the presence of organic matter will greatly increase adsorption, but organic matter is very low in the Ogallala.

Pore size and pore concentration in an aquifer will affect the adsorption characteristics because of their influence on adsorbate-adsorbent distances and their influence on the rate of flow past any given particle. It would appear from a mass action and solubility standpoint that the greater the volume of water moving past a point in a given unit of time, the greater will be the desorption.

Temperature and pH are also likely to be of importance in the adsorption of pesticides in an aquifer. Generally, such adsorption would be expected to increase with decreases in both temperature and pH.

Finally, the nature of the adsorbate will obviously be a primary factor in determining the degree of adsorption. Different pesticides will be adsorbed to different degrees on identical adsorbents because of differences in the chemical structures of pesticide molecules and the resulting variations in affinities for adsorbent and solute. It seems probable that within a given family of pesticides the adsorption will be inversely proportional to water solubility.

DDT was chosen as a representative pesticide for use in this study because of its relatively low toxicity, its persistence, and

its membership in the family of chlorinated hydrocarbons which are widely used. If the factors likely to affect adsorption of pesticides are carefully considered, it is believed that results obtained in this investigation may be employed as a guideline in considering the possible fate of other chlorinated hydrocarbons such as dieldrin and endrin under similar conditions.

Nitrates in Ground Water

Nitrates were incorporated in this study because of the health aspects in regard to both humans and animals.

The cause of infant cyanosis (methemoglobinemia) or blue babies has long been attributed to nitrates in water supplies.[6,7] In this case, nitrate is first converted to nitrite in the intestinal tract; the nitrite is then absorbed into the blood stream where it combines with hemoglobin, thus depriving the organs and tissues of needed oxygen.

In addition, there is evidence that high nitrate water can produce intestinal pathological conditions resulting in chemical diarrhea.[8]

For human consumption, the U. S. Public Health Service has established drinking water limits of 45 mg/l nitrates. There is, however, increasing evidence that even this limit can significantly affect both animals and humans, and some reports show harmful effect with concentrations as low as 5 mg/l.[9,10]

Nitrates occur in almost all natural waters.[11] Concentrations range up to hundreds of mg/l; but, except when contamination is present, they seldom exceed 20 mg/l, with 10 mg/l or greater often regarded as a probable indication of sewage contamination.

The use of nitrogen fertilizers accounts for 30% of our food production.[12,13] Such widespread use has caused some speculation as to possible pollution of surface and ground water from the application or over-application of nitrogen fertilizers.[14,15]

The nitrate ion does not readily adsorb but, rather, moves freely through the aquifer. Although movement is not completely free, inhibition by the aquifer material is minute. The presence of anaerobic bacteria can convert nitrates to nitrites so that less nitrate will be recovered from a system than is added to it. It is generally believed that these bacteria are not normally active in aquifers, especially at depths characteristic of the Ogallala, and would be expected to have little effect on the nitrate content of the water.

Areal Description of the Ogallala Formation

The Ogallala Formation is truly one of the large ground-water reservoirs of the world. Paralleling the eastern front of the Rocky Mountains, it extends from southern South Dakota to southwest Texas, a distance of some 825 miles. East to west, it averages about 190 miles in width. Its total area of about 158,000 square miles covers

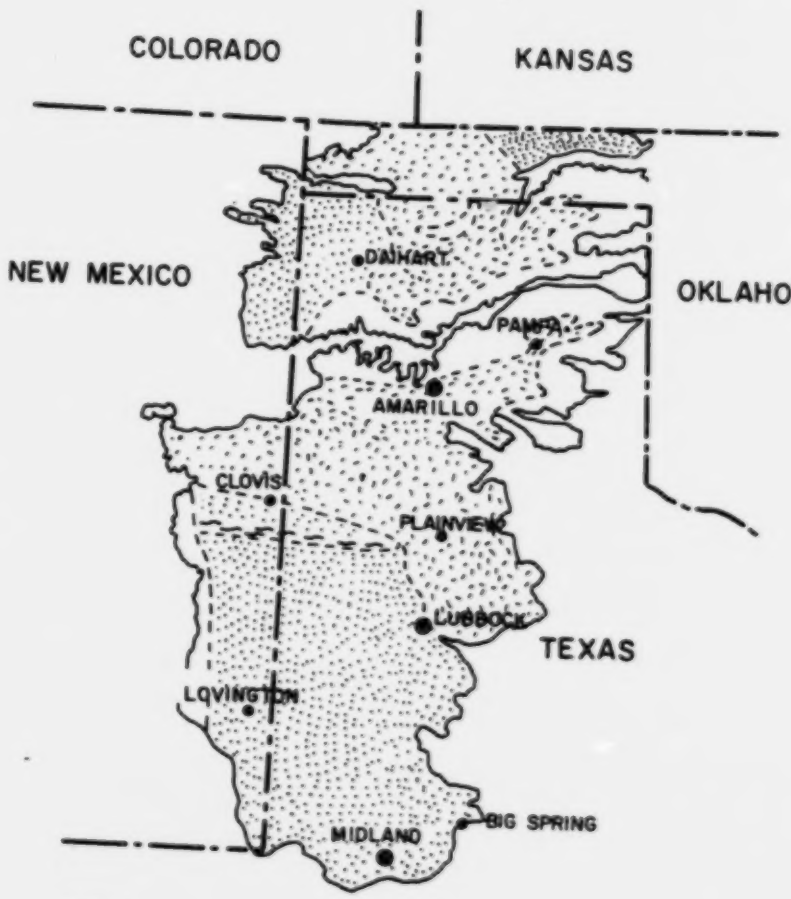
parts of Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Wyoming, and Texas. This total area is about the size of the state of California.

Although these figures of geographic expanse are highly impressive, the formation is also of great economic importance to its region in that it is the principal source of fresh water and because much of its surface exposure is comprised of rich, level soils highly suited to irrigated agriculture. Because of this combination of water and soils, in recent years the region has been developed into one of the largest and more productive irrigation areas in the nation.

Since current data on overall development and use of ground water from the Ogallala Formation are not readily available, the situation in the High Plains of Texas, south of the Canadian River, will be discussed briefly to illustrate the economic significance of the Formation. The Ogallala covers 24,800 square miles in this area as shown in Figure I-1. Rayner[16] in 1965 reported that about 45,000 irrigation wells, 650 municipal wells and 400 industrial water supply wells are developed in this part of the Ogallala, and about four million acre-feet of water per year is pumped from these wells--an amount four times the total annual use for the state of Oklahoma.

Water-yielding characteristics of the Ogallala are adequate for development of large-capacity wells throughout its geographic extent except in those areas where river valleys dissect the formation and

C-A



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SOUTHERN OGALLALA FORMATION

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FIGURE I-1

in certain localities where water-saturated thickness of the formation is thin or nonexistent. The formation consists of river-deposited clay, silt, sand, and gravel. Even though continuity of layering is difficult to trace for more than a few miles, the physical appearance of the formation from one locality to another is surprisingly similar. For example, the outcrop near Ogallala, Nebraska, where the formation was officially first described and from which town its name is derived, very much resembles formation outcrops in the eastern escarpment of the High Plains east of Lubbock, Texas.

However, hydraulic characteristics of the formation may vary greatly from one locality to another. Such variations often result from differences in saturated thickness, but more often result from the presence of beds of well sorted coarse materials such as sand and gravel.

II. FIELD INSTRUMENTATION AND PROCEDURES

Physical Description

This research was conducted at the Southwestern Great Plains Research Center at Bushland, Texas. Recharge and observation wells were located in a large playa depression near the edge of a dry playa lake as shown in Figures II-1 and II-2. The bottom of this lake consists of an impermeable clay layer which varies in thickness from 4 to 30 feet and prevents or greatly inhibits vertical percolation into the soil and ground water.

The recharge water was supplied by an irrigation well located 2,280 feet northeast of the recharge area. Water from this source well was transported by irrigation pipe through two parallel sand traps, two propeller meters, and into the recharge well. The sand filters collected several hundred pounds of sand from the recharge water, preventing possible filling of the recharge well.

A constant head of 5 psi at the point of injection was maintained in the injection pipes at the ground surface by an overflow pipe located near the sand traps.

Two chemical mixing tanks were alternately connected to a piston-type chemical feed pump which delivered about three gallons per hour of nitrate, DDT, tritium and water mixture to the recharge pipe as shown in Figure II-3. A mixing chamber containing an auger

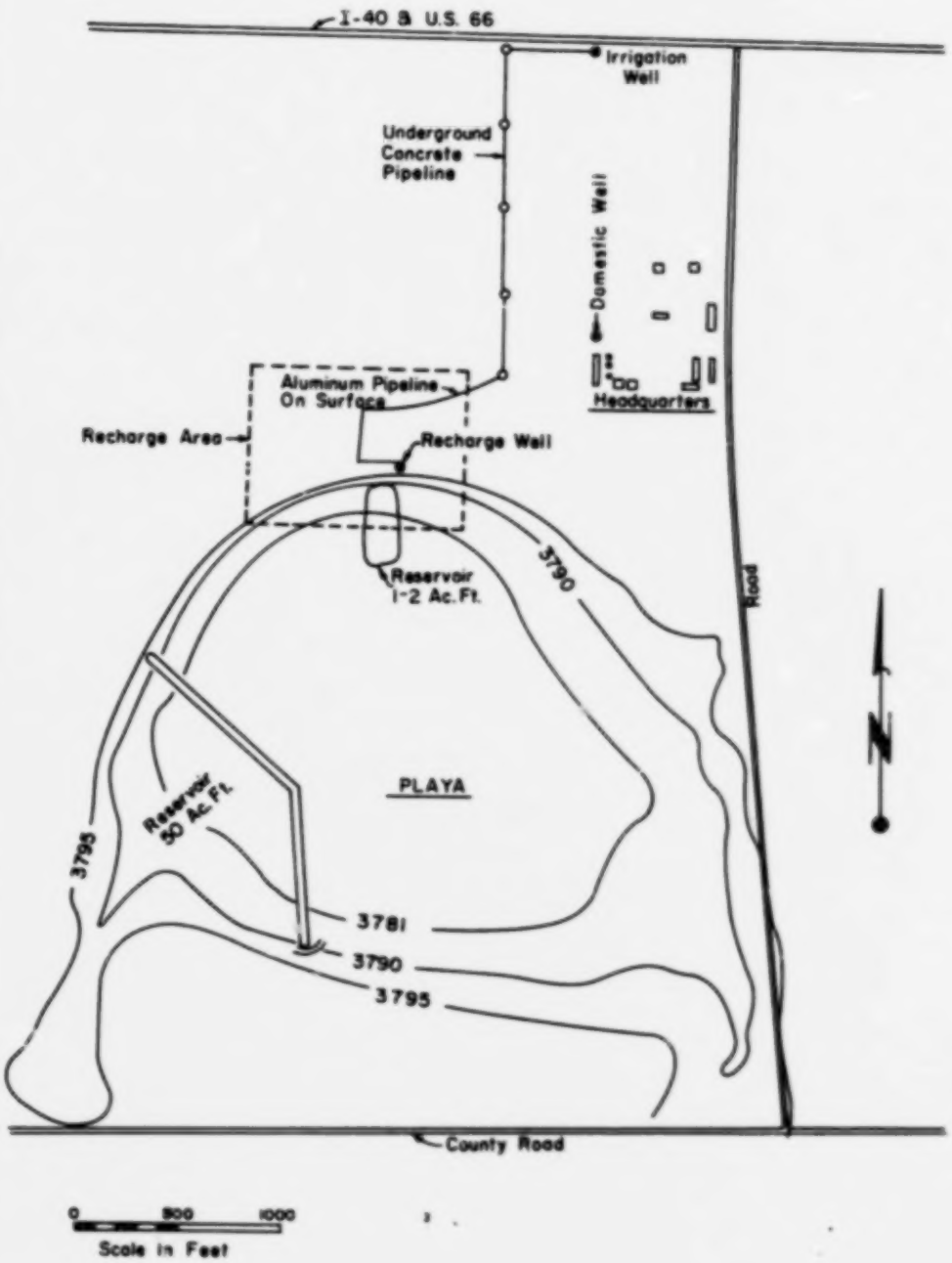

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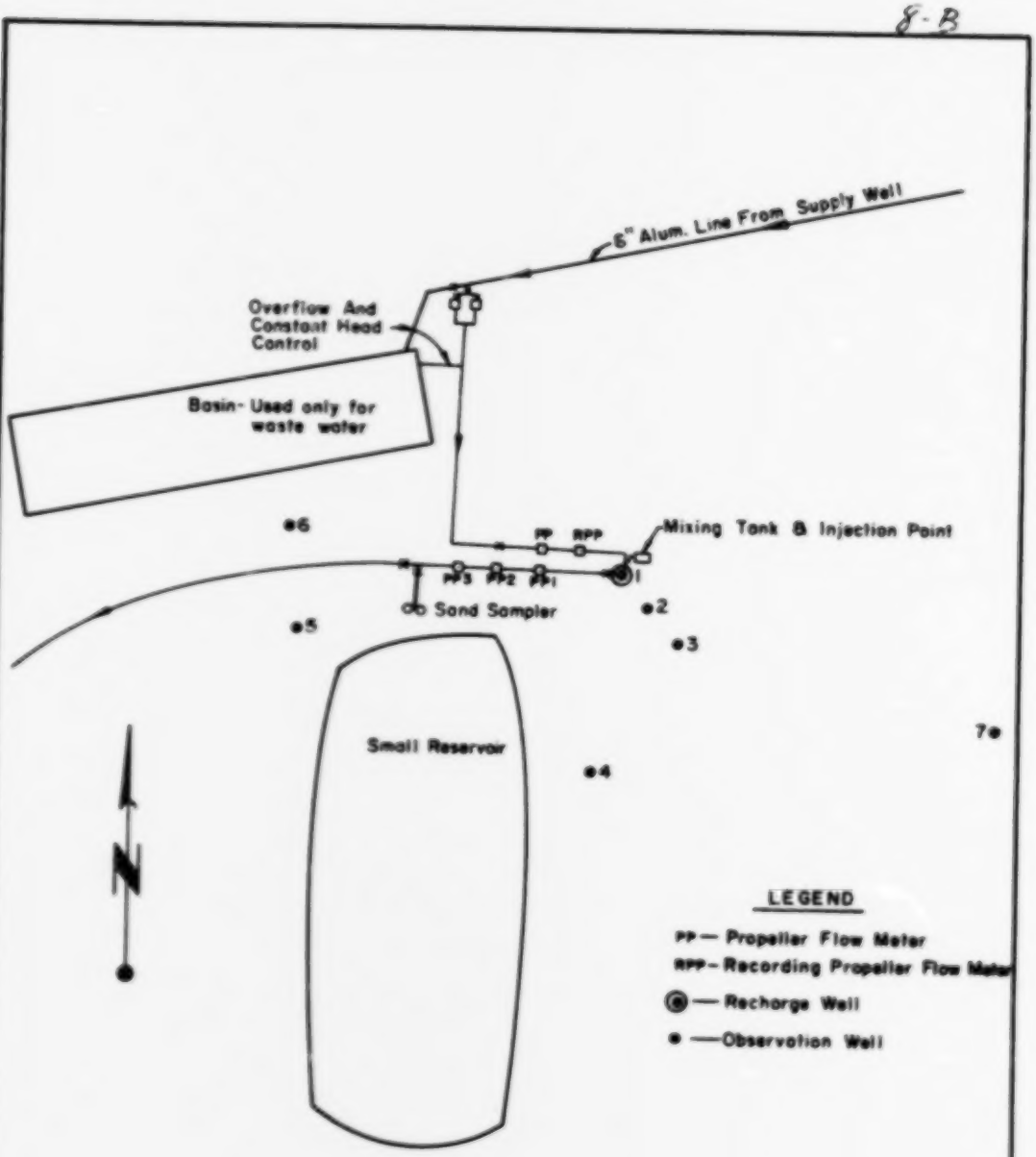
FIGURE II-1



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LOCATION MAP OF FIELD SITE

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FIGURE II-2

8-C

FATE OF DDT AND NITRATE IN GROUND WATER

CHEMICAL FEED SYSTEM

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FIGURE 11-3

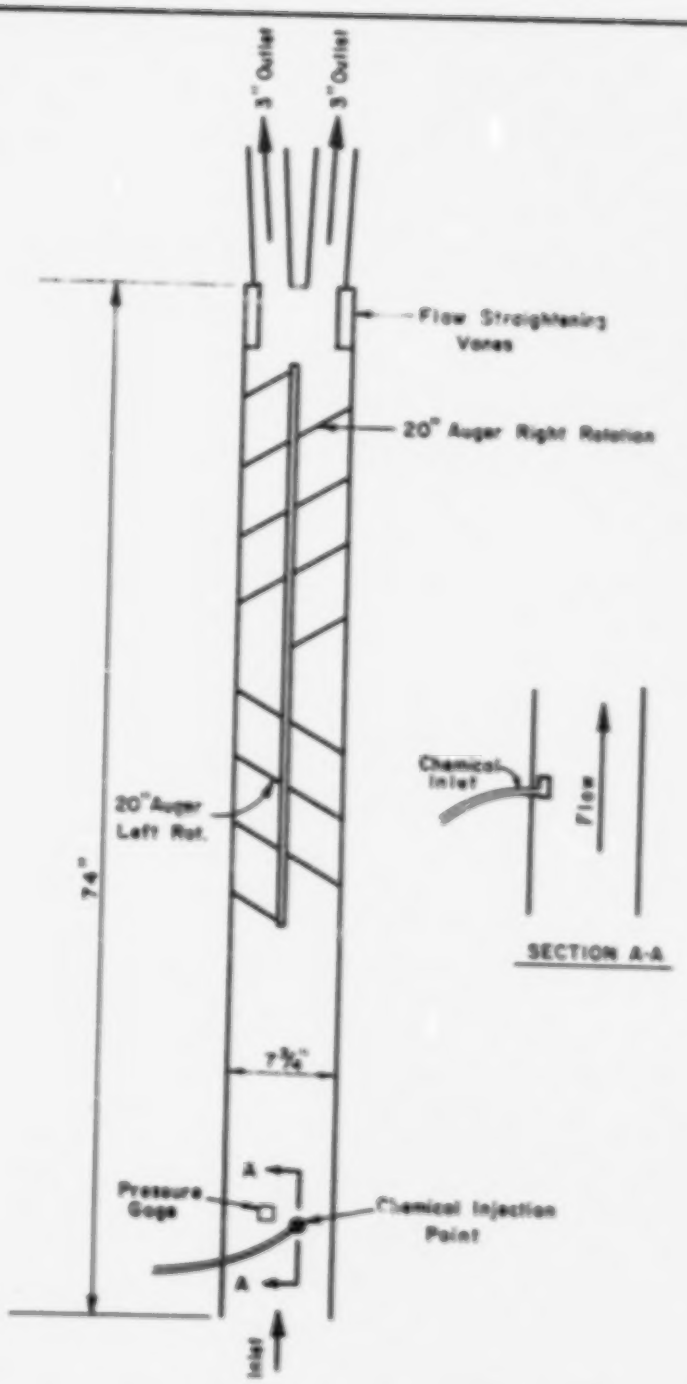
system shown in Figure II-4, immediately provided turbulence for mixing the pollutants and tracer with the recharge water before injection into the recharge well.

Recharge of the well was through two 2-inch pipes connected to the mixing chamber and terminating 145 feet below the ground surface. During recharge operations, the ends of both pipes were submerged in the well at all times. Figure II-5 presents a cross section of the recharge well and injection pipes. To prevent air entrainment difficulties, it was necessary to maintain a positive pressure at all points in the injection system. A streamlined plug was suspended on a cable from the end of each pipe, and the plug was positioned so as to maintain this positive pressure.

The recharge-pumping well was equipped with a water-lubricated deep-well turbine pump powered by a V8 internal combustion engine. This system had a pumping capacity of more than 1,000 gpm for prolonged periods of time.

Instrumentation

Two propeller-type meters were used to measure the flow rate of the recharge water. One of the meters was connected to a recording rate meter which maintained a continuous record of the flow throughout the 22-day recharge-pumping period. A third meter was also used in measuring the flow rate during the pumping phase of the experiment. The differences in measurements between the different meters were within the factory specified plus or minus 2 percent precision for the meters.



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CROSS-SECTION OF MIXING CHAMBER

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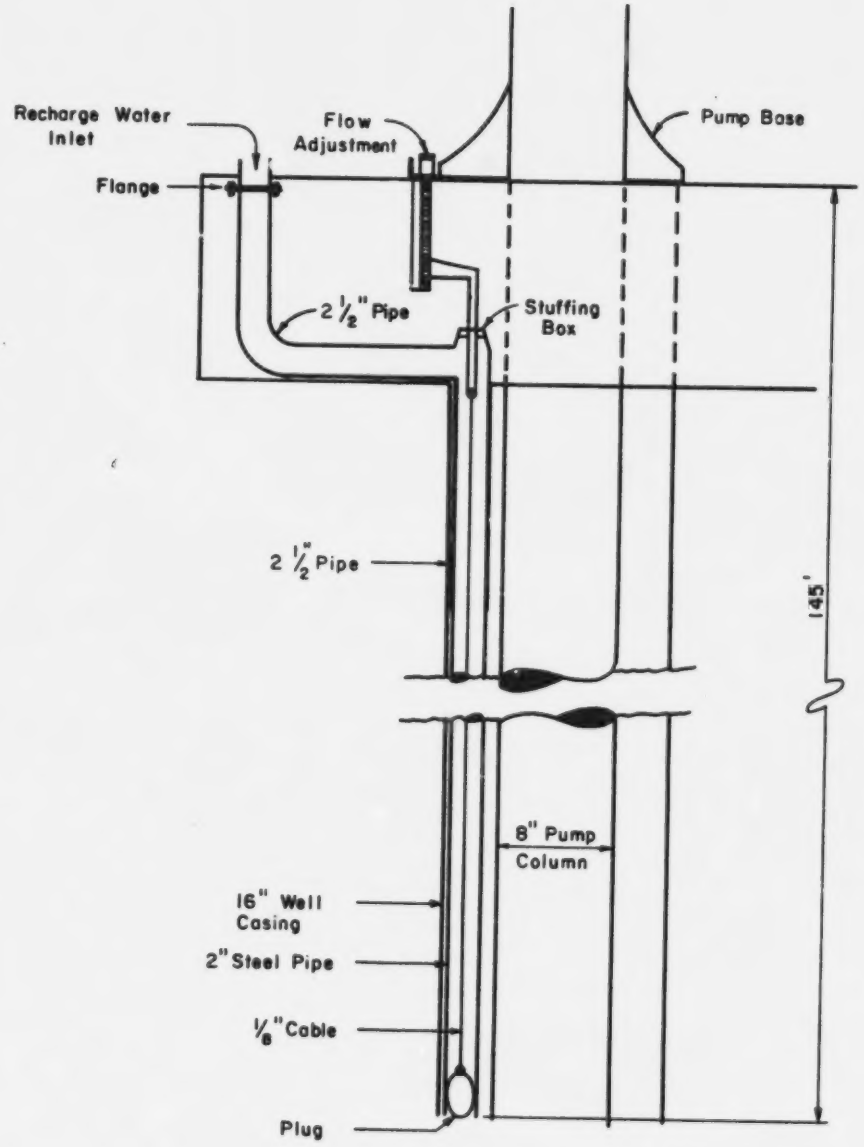
FIGURE II-4



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CROSS-SECTION OF RECHARGE - PUMPING WELL

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FIGURE II - 5

Float-operated water level recorders were used continuously in Wells No. 5 and 7 and four others located between 250 and 1,000 feet from the recharge well. Water levels were measured in Wells No. 3, 4, and 6 several times each day with an electric well sounder. This method was also used on five other wells in the test area. Air-operated bubbler-gauge recorders were used to record water levels in Well No. 1 and in a 2-inch well located 90 feet south.

To measure the sand produced by Well No. 1 during the pumping phase of the experiment, the flow was diverted through a "T" and into a slot type sampler shown in Figure II-6.

Well Construction

Well No. 1, the recharge-pumping well, was drilled 28 inches in diameter and 269 feet in depth by conventional hydraulic rotary drilling methods. The well screen and 1/4-inch casing were 16 inches in outside diameter. Continuously wound galvanized steel wire screen spanned 90 feet of the well from 161 to 253 feet below the ground surface, terminating above the clay layer. Gravel pack, designed to hold the formation in place during pumping or recharge, filled the annulus around the well screen. Concrete filled 16 feet of the casing below the screen and extended into the clay layer. Concrete was also placed between the casing and the drilled hole from the surface to a depth of 92 feet.

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SLOT TYPE SAND SAMPLER

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FIGURE 11-6

Observation Wells No. 2 through 7 were drilled by conventional hydraulic rotary drilling methods to depths ranging from 270 to 354 feet and were lined with 6-inch casings. All casings except Well No. 4 were slotted by acetylene cutting torch from about 100 feet below the surface to depths ranging from 265 to 354 feet and surrounded by gravel pack. Well No. 4 had special factory made casing slots, from 160 to 260 feet below the surface, designed to hold back formation sand without gravel pack.

Wells No. 1, 3, and 5 had been used in previous experiments by USDA for recharge of playa lake water.[17,18] Following these operations, bailing of the wells produced several cubic yards of sand. Cavities created outside Wells No. 3 and 5 were later filled with gravel.

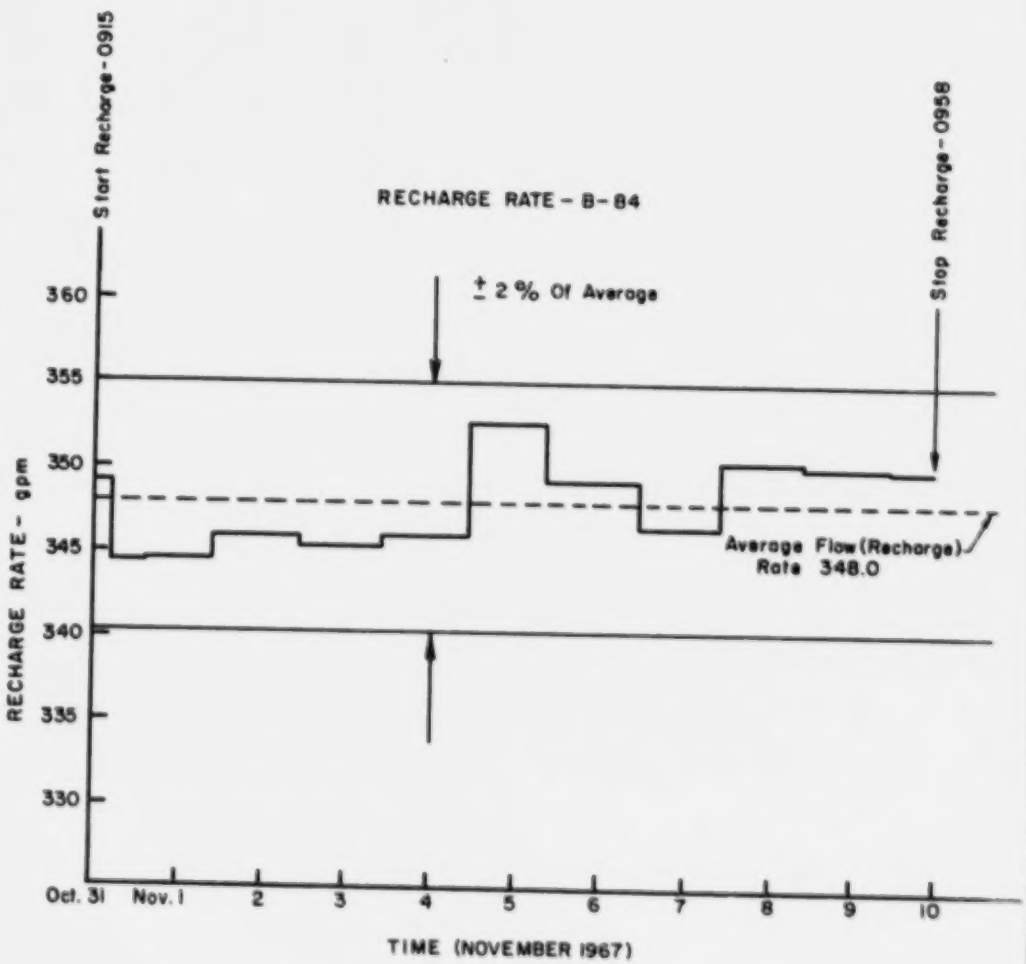
Several 2-inch wells in the vicinity of the recharge well were used for water level measurements. These wells were developed by air-lift pumping and consisted of a 2-inch pipe and 2-inch by 2-foot well points installed inside a 4 1/2-inch drilled hole. Water level response was the same as that in the 6-inch wells which fully penetrated the aquifer.

Injection and Pumping Procedures

On the day before the project started, water was recharged into the injection well for a few hours to adjust all the flow control equipment and minimize start-up adjustments.

Recharge started at 9:15 a.m. on October 31, 1967, and addition of pollutants started at 10:00 a.m. of the same day. Recharge continued at a 10-day average rate of 348 gpm, with fluctuations within plus or minus 2 percent (Figure II-7), until 9:58 a.m. on November 10, 1967.

Following the 10 days of recharge, the well was allowed to sit idle for 3 hours; pumping started at 1:00 p.m. on November 10. Water was pumped continuously from the recharge well at an average rate of 504 gpm, plus or minus 2 percent, until 1:00 p.m. on November 22, 1967. The pumped water was transported by pipeline to a clay bottomed reservoir and allowed to evaporate.



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RECHARGE RATE OF RECHARGE-PUMPING WELL

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FIGURE II-7

III. HYDRAULICS AND GEOLOGY

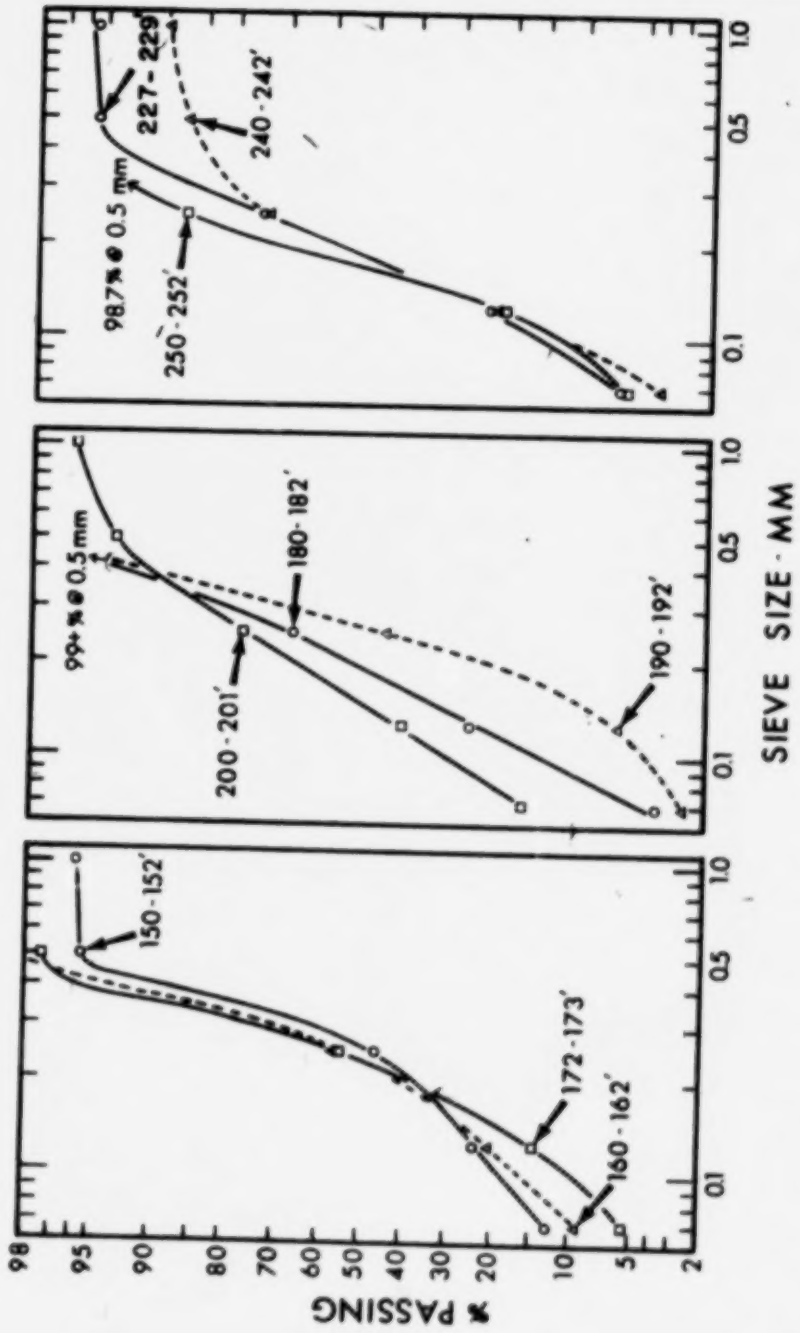
Hydrogeology of the Field Site

The Ogallala Aquifer at the test location is bounded on the top by caprock at a mean sea level (MSL) elevation of 3,768.3 feet. The sandstone caprock, cemented primarily with calcium carbonate, is about two feet thick over all the area influenced by this experiment. In October 1967, the water table stood at a MSL elevation of 3,635.3 feet, leaving 133 feet--or more than one-half of the Ogallala--unsaturated.

The bottom of the aquifer at the test site consists of a dense clay layer of extremely low permeability. This clay layer has been found to be at least three feet thick in all test wells within 1,500 feet of the recharge well. Although the top of clay is not horizontal, the elevation varies less than five feet within a 500-foot radius of the recharge well.

The aquifer in the test area is comprised primarily of fine sand. There are numerous thin layers and nodules of sand cemented with calcium carbonate and other acid-soluble cementing agents. Figure III-1 presents the particle-size distribution of undisturbed core samples from below the present water table in a test hole 66 feet southwest of Well No. 1. The distributions shown were obtained without crushing so as to retain cemented nodules in their original size and shape.

These nodules vary in size from two sand grains up to one or two feet in diameter and have been observed in undisturbed cores and in



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PARTICLE SIZE DISTRIBUTION

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FIGURE III-1

places in the walls of shafts down to 95 feet below the ground surface. Particle sizes were determined from one set of core samples by two different methods. The first group was wet-sieved to preserve cemented nodules in their natural state while the second group of samples was dried and crushed with a rubber roller in a steel pan. Table III-1 presents the difference in percent by weight larger than 0.841 millimeter in diameter.

Laboratory permeability, particle size distribution, and carbonate content from representative core samples are presented in Table III-2. All of more than 100 core samples analyzed from the test aquifer contained more than one percent by weight of clay. Permeability determined from cores, electric and gamma ray well logs, and driller's logs indicates a highly stratified aquifer with a greatly variable permeability over short vertical distances. Figure III-2 presents electric and gamma logs from the test well 66 feet southwest of Well No. 1.

Hydraulics

Investigations of ground-water hydraulics necessarily involve the parameters of permeability, transmissibility, and storage.

1. Coefficient of permeability (P) is defined as the number of gallons per day flowing through an area of 1 square foot under a hydraulic gradient of unity (1 ft/ft) and maintains units of gallons per day per foot^2.

Table III-1

Wet and Dry Sieve Comparison

Depth (ft.)	Percent Larger Than 0.841 mm	
	Wet Sieve* (%)	Dry Sieve** (crushed) (%)
150-152	4.2	0.2
160-162	<0.9	0.0
172-173	2.2	0.6
180-182	<0.75	0.0
190-192	<0.27	0.0
200-201	4.0	1.3
227-229	4.2	0.4
240-242	10.3	0.2
250-252	<1.3	0.2

*Wet sieve had minimum disturbance; the sample was washed through sieves larger than 0.5 mm, and the portion smaller than 0.5 mm was sieved dry.

**Dry sieve samples were crushed before dry sieving by a rubber roller on a steel surface. Quartz sand grains were not crushed.

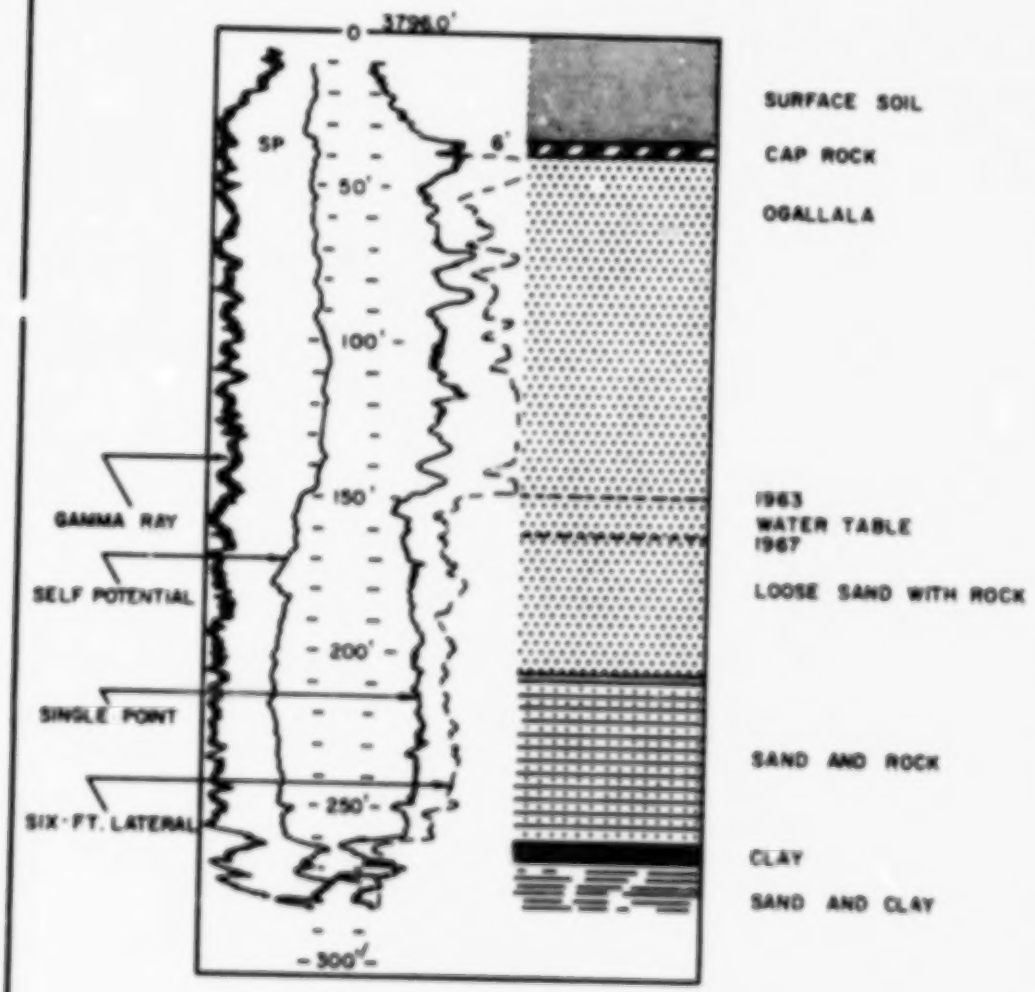
Table III-2

Core Analyses of Ogallala

Mean Sea Level Elevation (ft.)	K* (cm/day)	Sand >50μ (%)	Silt 2-50μ (%)	Clay >2μ (%)	CO_3 (%)	Comments**
1,401 feet south of recharge well						
3639.2 to 3637.2	155	87	5	1.4	6.6	Top
		75	4	1.4	19.6	Bottom
3618.2 to 3616.2	11	93	2	2.0	3.0	Top
		83	2	2.3	12.7	Bottom
3595.7 to 3595.2	30	95	2	1.2	1.8	---
1,049 feet west-southwest of recharge well						
3599.9 to 3597.9	0.8	92	3	2.7	2.3	---
3570.4 to 3568.4	29	85	4	2.4	8.6	---

*Permeability, cm/day.

**Indicates top or bottom of core; permeability is average for entire core.



FATE OF DDT AND NITRATE IN GROUND WATER

ELECTRIC AND GAMMA LOGS

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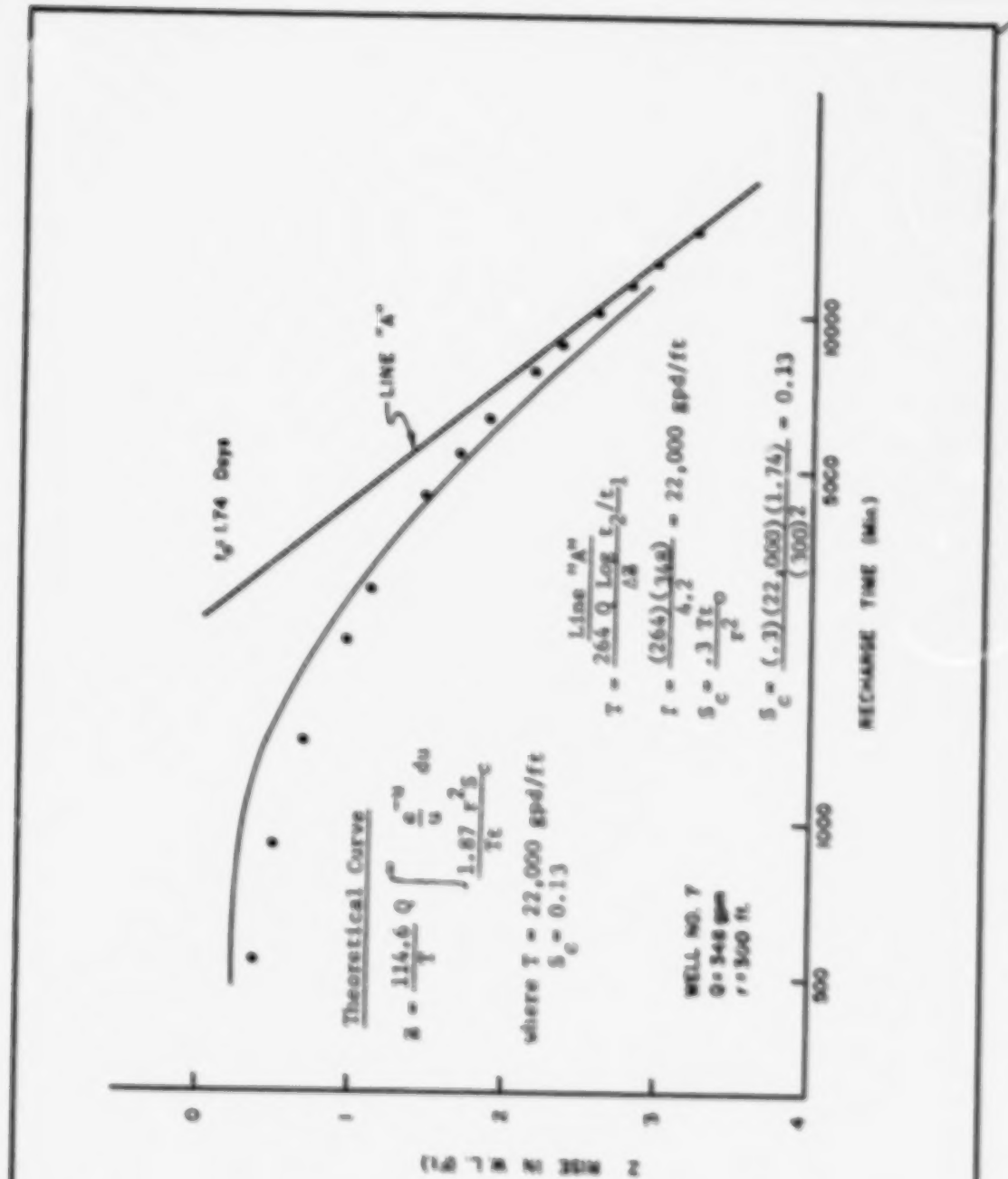
FIGURE III - 2

2. Coefficient of transmissibility (T) is defined as the number of gallons per day flowing through a vertical section of the aquifer 1 foot wide under a unit hydraulic gradient (1 ft/ft). It is therefore the product of the permeability coefficient and the aquifer's saturated depth in feet. The units are gallons per day per foot.
3. Coefficient of storage (S_c) is defined as the volume of water removed from a 1 square foot column of the aquifer when the water table is lowered 1 foot.

These coefficients were determined by the modified Theis formula[19] from the recharge portion of this project using water level observations at the recharge well and four selected observation wells. Storage coefficients calculated by this method varied from 0.05 at Well No. 2 to 0.13 at Well No. 7, and transmissibility coefficients ranged from 10,266 gpd/ft using water levels at the recharge well to 22,000 gpd/ft using levels at Well No. 7.

Solution of the Theis formula at Well No. 7, which most nearly satisfies necessary assumptions, is shown in Figure III-3. Storage and transmissibility coefficients compare favorably with those determined in previous recharge experiments at Bushland and with those reported by Moulder and Frazor.[20]



FATE OF DDT AND NITRATE IN GROUND WATER	
STORAGE AND TRANSMISSIBILITY BY MODIFIED THEIS FORMULA	
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FIGURE III - 3

There was wide variation in calculated coefficients at Bushland because observations failed to fit the theoretical formulations used. This departure has been reported by others, including Moulder and Frazor[21] who performed recharge tests on the Ogallala Aquifer nine miles east of the Bushland site. These authors attribute theoretical departures to slow filling of the aquifer during recharge and to the magnitude of the water level rise in relation to the aquifer's saturated depth. They concluded that conformance to theoretical consideration was more closely achieved after longer recharge periods and at greater distances from the recharge well. This conformance would only be realized at some time greater than that used in this project.

Moulder and Frazor best pointed out the possible inadequacies in using this approach to describe this aquifer's characteristics:

> Conditions during the tests departed markedly from the conditions set forth in the derivation of the analytical equations; therefore, the determinations of aquifer coefficients are subject to considerable error. For example, slow drainage or slow filling of sediments with water made the data collected early in the tests unusable for analysis by the nonequilibrium method. Conformance to theoretical conditions takes longer times at greater distances from the pumping or recharging well. Adjustments to the basic data may be made to correct or compensate for such things as regional water-level trends and changes in saturated thickness of the aquifer, but the success of these adjustments in determining the true aquifer coefficients is dependent largely upon the agreement between field conditions and the conditions assumed by the adjustments.[20]

At Bushland, another method was employed to calculate the storage coefficients. Using detention times calculated from tracer

studies described in Section V of this report, storage coefficients of 0.23 and 0.20 were calculated from the detention times of tritium and nitrates, respectively, between recharge and observation wells. These values are believed to be reliable since the method of calculation is relatively insensitive to reasonable variations in detention time and aquifer depth. Also, these values are not subject to the numerous assumptions required for the pump test method and which are not usually met in practice. In addition, these higher values agree with storage coefficients found by the USDA at Bushland in laboratory studies of 100 undisturbed cores of the aquifer.

IV. POLLUTIONAL PARAMETERS

Recharge of Pollutants

Artificial recharge operations in the High Plains normally employ, as a source of recharge water, rainfall collected in playa lakes common to this area. Because suspended matter often causes clogging of the recharge wells, clarification is sometimes needed before these waters can be recharged. In addition, other pollutants may be present in various and significant concentrations.

To avoid this problem and because the supply of playa lake water at Bushland, Texas was limited, an irrigation well was used as the only source of recharge water for this project.

The recharge rate was maintained at 348 gallons per minute for the full 10-day period. This rate is representative of recharge practices in the High Plains. Nitrate was added to the recharge water at a weighted average rate of 24.4 mg/l, including the 7.7 mg/l background from the supply well, and p,p'-DDT was added at an average rate of 74 parts per billion (ppb). Over the total recharge period, this concentration amounted to 1,028 and 3.11 pounds of nitrates and DDT, respectively. In addition, four curies of tritiated water were added as a tracer at a rate of 210 micromicrocuries per milliliter (μμc/ml).

Tracer, nitrate, and DDT were received in the form of tritiated water, industrial grade sodium nitrate, and commercial grade 50 percent wettable DDT powder, respectively. Suitable quantities of all three were added daily to one of two mixing barrels and diluted to about 80 gallons. An electric motor was used to power a mixing paddle in each barrel in order to maintain the DDT in suspension. The contents of each barrel were agitated overnight and during a subsequent feed period of about 24 hours.

Methods of Sampling

Sampling was confined primarily to Well No. 1, the recharge well, and Observation Wells No. 2, 3, and 4 located at radial distances of 33, 66, and 150 feet, respectively, from the point of recharge. Occasionally, samples were taken from wells at greater distances. These wells included the domestic water supply for the agricultural experiment station at Bushland. Samples taken from distances greater than 150 feet were collected primarily for background information and as a safety precaution and were generally analyzed only for tracer concentrations.

During the 10-day recharge period, samples designated Well No. 1 represented recharge water after mixing with the pollutants and tracer and were taken from the top of the recharge well through a manometer tube. During the pumping period, Well No. 1 samples were taken immediately on the effluent side of the pump.

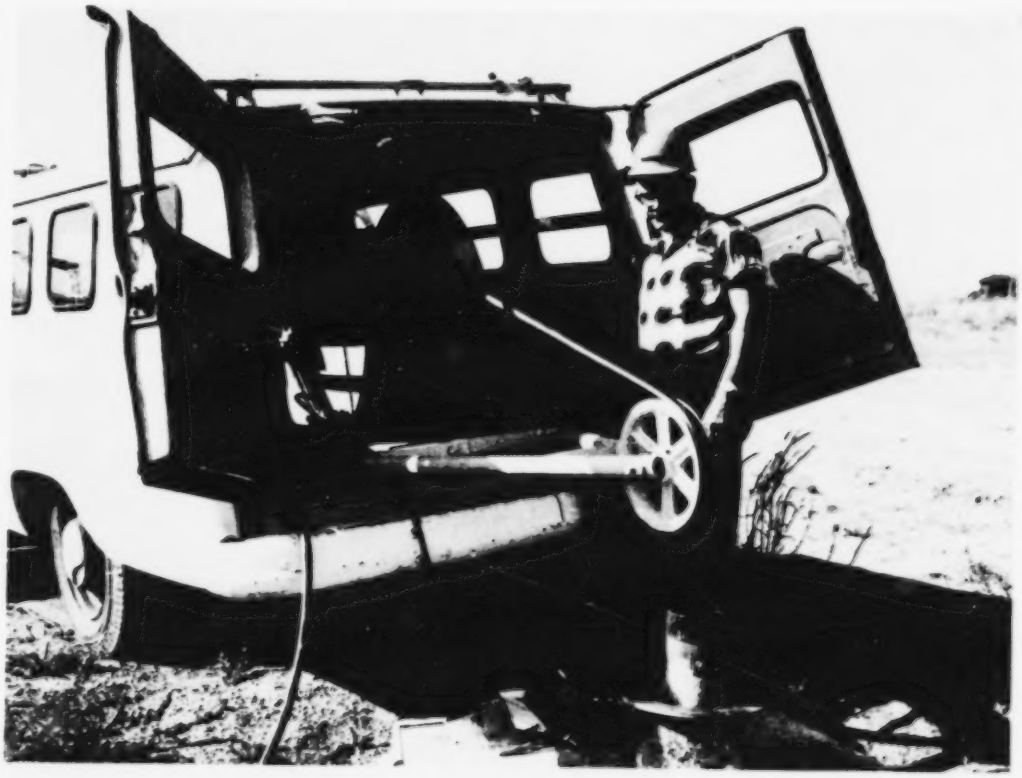
Observation wells were sampled with the portable pump system shown in Figure IV-1.[21] The system consisted of a submersible pump which was lowered or raised in an observation well, using a hose on an electric winch and spool assembly. The sampling depth was about 190 feet below the ground surface (approximately 30 feet below static water level) in all the observation wells. Before each sampling, the well was purged for 30 minutes by pumping at 10 gallons per minute. This time was sufficient to withdraw about three times the volume of water in the well and was believed to provide a representative sample of the aquifer at that location.

To reduce the quantity of sand and other particulate matter in the aqueous samples during collection, the sample stream was passed through a Tyler equivalent mesh No. 270 (53 microns or 0.0021 inches) standard eight-inch brass sieve. The sample stream was directed at the side of the sieve so that the water moved across the screen rather than directly through it; this reduced forcing of particulate matter through the sieve by hydrostatic pressure.

Samples were collected in one-quart glass jars with teflon-lined lids. These jars and teflon liners were previously washed thoroughly with dichromate cleaning solution, tap water, and distilled water.

Great care was exercised during sampling to prevent contamination of samples with substances which would interfere with DDT analysis.

Sand samples for the determination of adsorbed DDT were taken from the pumped stream in the cleansed one-quart jars. They were



FATE OF DDT AND NITRATE IN GROUND WATER

PORTABLE PUMP SYSTEM

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FIGURE IV-1

obtained simply by collecting the unfiltered stream and decanting after the particulate matter had settled.

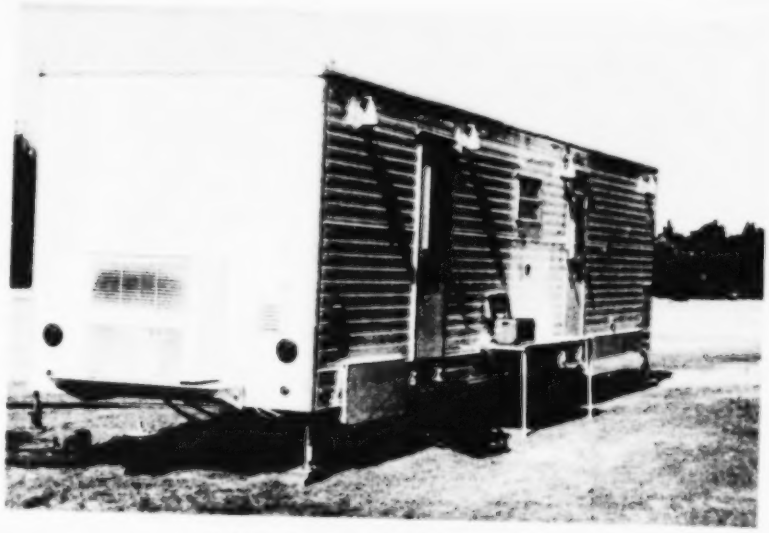
Methods of Analyses

Analyses for tritium, nitrates, and DDT were conducted in a mobile laboratory (Figures IV-2 and IV-3) of the Robert S. Kerr Water Research Center.

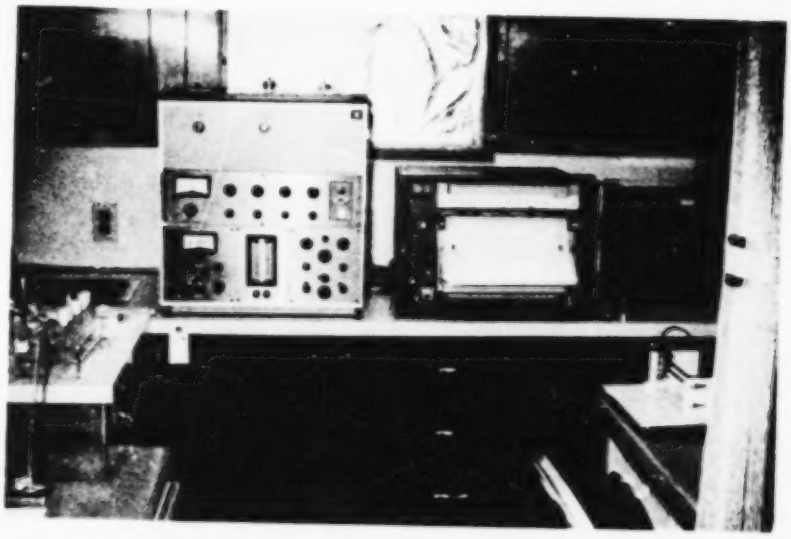
Nitrite and nitrate nitrogen were determined by use of a Technicon AutoAnalyzer[22] following the automated technique described by Kamphake, Hannah, and Cohen.[23] All samples were analyzed immediately after collection to reduce any errors arising from changes in the nitrogen balance. Standards were analyzed before and during each day's run for accuracy. At intervals, duplicate samples were compared for reproducibility of results.

All samples were analyzed for tritium with a Beckman Model LS-150 Liquid Scintillation Spectrometer.

The methods employed for quantitative analysis of DDT in the various water samples were essentially those described by Breidenbach et al,[24] with some modification. Samples of 600 to 800 ml of water were extracted twice consecutively by stirring for 30 minutes each time with 35 ml portions of hexane. Extractions were conducted in the original quart sample bottles with teflon-lined lids, using two-inch teflon-coated magnetic stirring bars. After each extraction, the hexane and water phases were separated in one



Outside View Of Mobile Laboratory



GAS CHROMATOGRAPH SYSTEM - Used For DDT Analyses

FATE OF DDT AND NITRATE IN GROUND WATER

MOBILE LABORATORY AND GAS CHROMATOGRAPH

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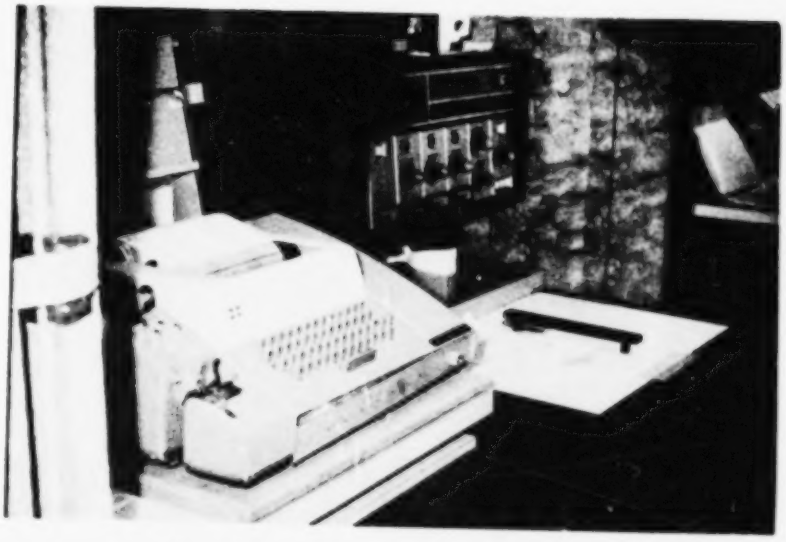
FIGURE IV-2

AUTO ANALYZER- Used For Nitrate And Nitrite Determination



LIQUID SCINTILLATION SYSTEM- Used For Tritium Measurements

FATE OF DDT AND NITRATE IN GROUND WATER

AUTO ANALYZER AND LIQUID SCINTILLATION SYSTEM

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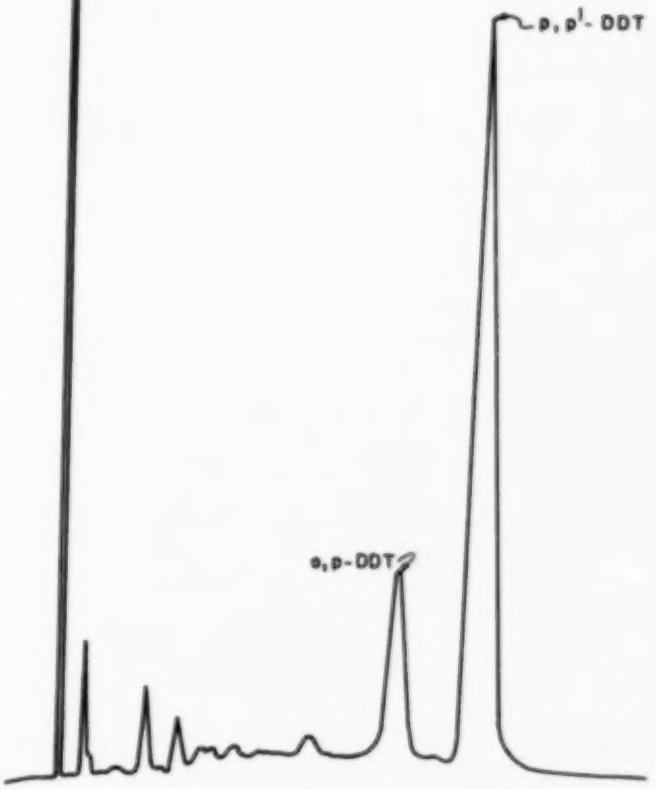
FIGURE IV-3

liter separatory funnels and the combined hexane extracts were dried by passing through 2" x 7/8" columns of anhydrous sodium sulfate. Extracts of samples from recharge stream and pumped water, in which DDT concentrations were relatively high, were adjusted to appropriate volumes and subjected to analysis by electron capture gas chromatography without further treatment. Extracts of samples from observation wells which contained low levels of DDT were subjected to thin-layer chromatography before quantitation of DDT in order to minimize interference by other extract components during the gas chromatography step. In this procedure, the extracts were evaporated to 2 to 8 ml volume, transferred to 15 ml centrifuge tubes, and further evaporated carefully to dryness under a gentle stream of air or nitrogen in a water bath at 40°C. The residues were dissolved in 100 µl of pure hexane; and 50 µl aliquots, together with standard DDT samples, were chromatographed on thin-layers of Adsorbosil 1 (Applied Science Laboratories, State College, Pennsylvania) with carbon tetrachloride as developing solvent. After locating zones containing DDT by spraying the standards with Rhodamine B, these zones were removed from the thin-layers by means of a microvacuum cleaner apparatus,[25] and the DDT was eluted directly into 15 ml conical centrifuge tubes with 5 to 6 ml of petroleum ether-diethyl ether mixture (1:1). The solvent was gently evaporated from these eluates, and the residues were dissolved in appropriate quantities (usually 100 to 500 µl) of pure hexane and subjected to gas chromatography.

For gas chromatography, a Varian-Aerograph Model 204B gas chromatograph equipped with tritium-foil electron capture detector and Minneapolis-Honeywell Model 16 recorder with Disc integrator was employed. A 5' x 1/8" stainless steel column packed with 5.4% DC-200 on 80/100 mesh Gas Chrom Q (Applied Science Laboratories, State College, Pennsylvania) was used for most analyses. In order to confirm identity of peaks, a 5' x 1/8" glass column packed with 5% QF-1 on 100/120 Aeropak 30 (Varian-Aerograph, Walnut Creek, California) was employed for analysis of a few samples. Essential operating parameters were: column temperature, 205°; injection port temperature, 235°; detector temperature, 211°; carrier gas, N_2; flow rate, 40 ml/min. Figure IV-4 shows a typical chromatogram obtained in analysis of recharge water. This chromatogram reveals the presence of the two principal isomeric forms of dichlorodiphenyl-trichloroethane, p,p'-DDT [1,1,1 - trichloro - 2,2 - bis (p-chlorophenyl) ethane] and o,p-DDT [1,1,1 - trichloro - 2-o - chlorophenyl - 2 - p - chlorophenyl ethane]. These are shown structurally in Figure IV-5. In this research, only p,p'-DDT, which comprised approximately 80% of the total DDT isomers of the recharge stream, was determined routinely; and the term DDT as used in this report refers to the p,p' isomer only unless otherwise noted.



FATE OF DDT AND NITRATE IN GROUND WATER

GAS CHROMATOGRAM OBTAINED IN ANALYSIS OF RECHARGE WATER

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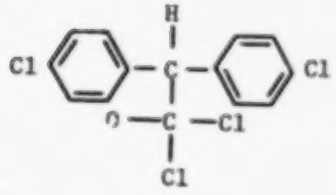
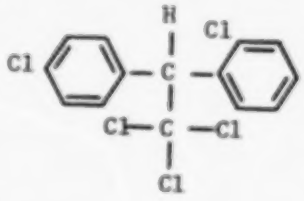
FIGURE IV-4

Figure IV-5

Structural Formula of Principal DDT Isomers



p,p'-DDT



o,p-DDT

Highly purified solvents were employed throughout the DDT analysis, and extensive precautions were taken to prevent contamination during the analytical procedures. Standard p,p'-DDT samples were routinely carried through the procedure with the unknowns to check recovery of DDT, which was found to vary from 70 to 98%. Correction of obtained DDT values to compensate for recovery efficiencies was not attempted.

For analysis of DDT adsorbed on sand samples, excess water was first decanted from the sample. The remaining aqueous sand slurry was then poured into a 22 mm diameter column equipped with fritted glass disc. The sand was washed with 350 to 500 ml of distilled water to remove all nonsorbed DDT and then was washed successively with two 100 ml portions of pure acetone and two 100 ml portions of pure hexane. The solvent was carefully evaporated from the acetone washings, and the residues were dissolved in pure hexane and dried with sodium sulfate. The resulting solutions and the

original hexane washings were adjusted to appropriate volumes and analyzed by electron capture gas chromatography, as previously described. The washed sand was dried and weighed to determine DDT adsorbed per unit weight of sand. This washing procedure appeared to be quite effective in removing adsorbed DDT from the sand since extraction of the previously washed sand in a Soxhlet extractor with acetone for 10 hours yielded no significant additional quantities of DDT. Essentially all of the adsorbed DDT was found to be removed from the sand by the first acetone wash.

V. RESULTS OF ANALYSES

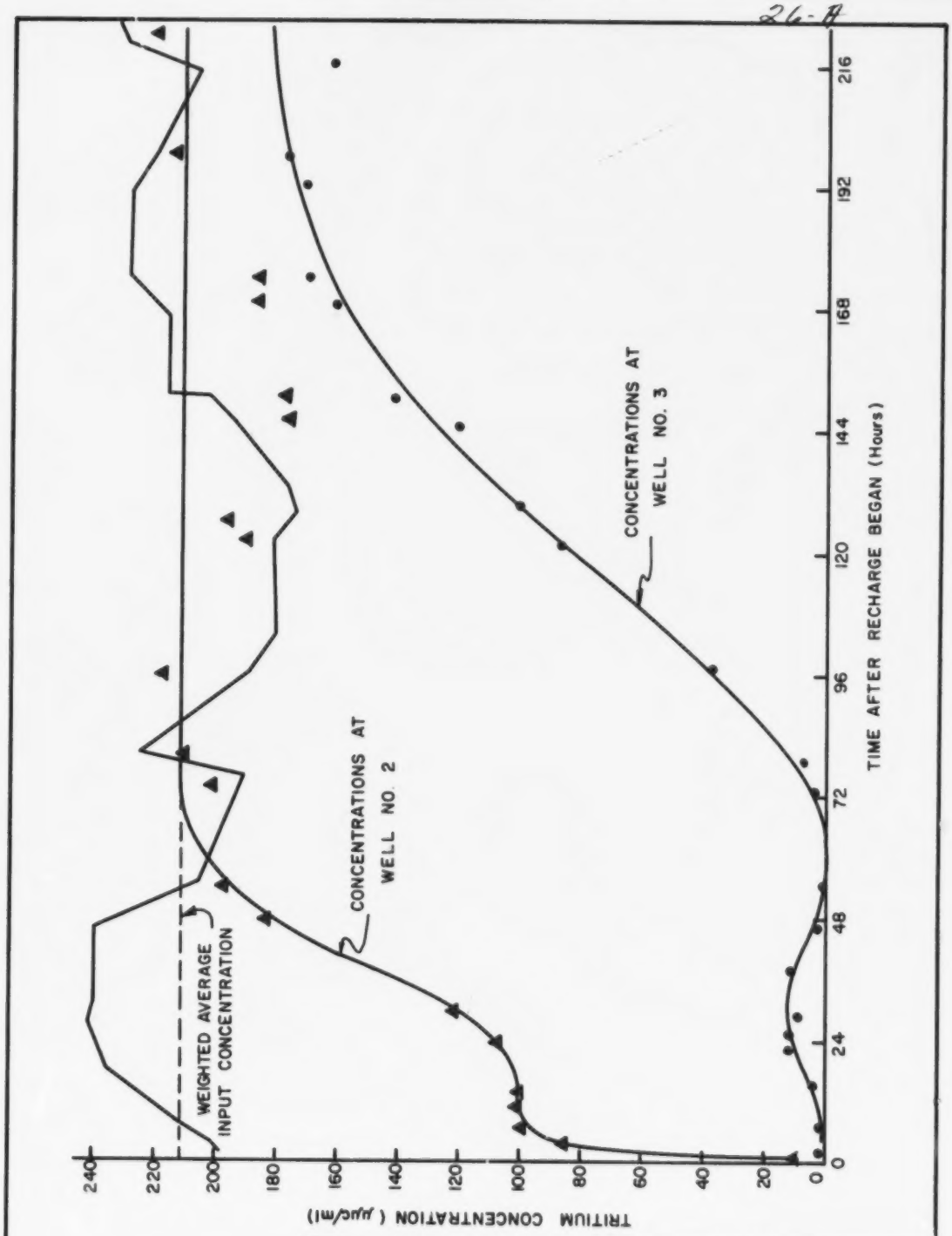
Tracer Recovery

Due to expected mixing and dilution of recharge water with water native to the aquifer, a tracer was necessary to determine the magnitude of these effects. The recharge water was tagged with tritiated water to determine the degree of dilution, the rate of movement of the recharge water, and the amount of recharge water recovered during pumping operations. Tritiated water was selected because its behavior is essentially chemically and physically identical to the water being studied.

By comparing tracer concentrations in observation wells with concentrations in the recharge water, it was possible to calculate the pollutant concentrations expected in the absence of breakdown, adsorption, or other losses in the aquifer.

Tritium was added to 348 gpm of recharge water at an average rate of 210 micromicrocuries per milliliter (μμc/ml) for 10 days as shown in Figure V-1. This injection rate resulted in a total of 4.0 curies being added to the ground water.

Tracer was recovered at Observation Wells No. 2 and 3 located 33 feet and 66 feet, respectively, from the recharge well. The native water in the aquifer between Well No. 2 and the recharge well was totally displaced after about three days of injection.



FATE OF DDT AND NITRATE IN GROUND WATER

TRACER DISPERSION DURING RECHARGE

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FIGURE V-1

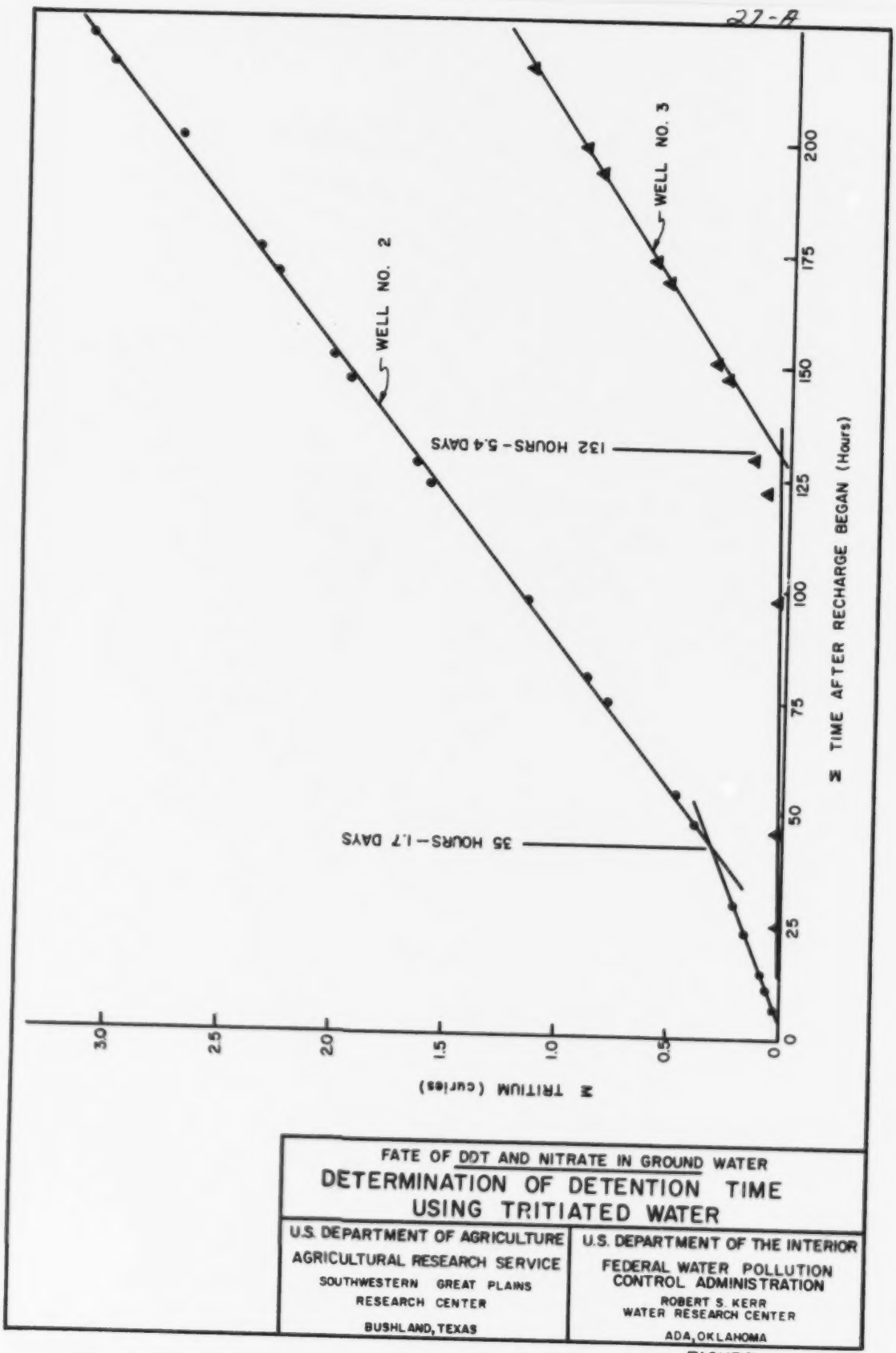
The native water in the aquifer between Well No. 3 and the recharge well was not completely displaced during this experiment as shown by the failure of the tritium concentration to reach the average recharge concentration. Part of this failure may be attributed to the low recharge concentrations noted on the fourth through sixth days as shown in Figure V-1. Tritium was not detected at all in Well No. 4 which was located 150 feet from the recharge well.

Detention times between the recharge well and observation wells were determined for use in calculation of aquifer storage coefficient mentioned in Section III and again in nitrate recovery.

The increase in tracer concentration at Wells No. 2 and 3 follow the normal ess-shaped curvature expected in these types of phenomena. The flow-through time, detention time, or geometric mean observation time to each of these wells is equal to the inflection point of their respective dispersion curves or to the second derivative of the formulation of these curves equated to zero.

Detention times were determined graphically in Figure V-2 by plotting the summation of tracer which had passed a radius, r, in time, t. This process involves two linear functions. The intersection of the two straight lines describes the flow-through or roughly the detention times.(26)

A more commonly used graphical solution is shown in Figure V-3 where the data are plotted on logarithmitic probability paper. A straight line fitted to the data intersects the 50 percentile concentration at the geometric mean observation time.



FATE OF DDT AND NITRATE IN GROUND WATER

DETERMINATION OF DETENTION TIME USING TRITIATED WATER

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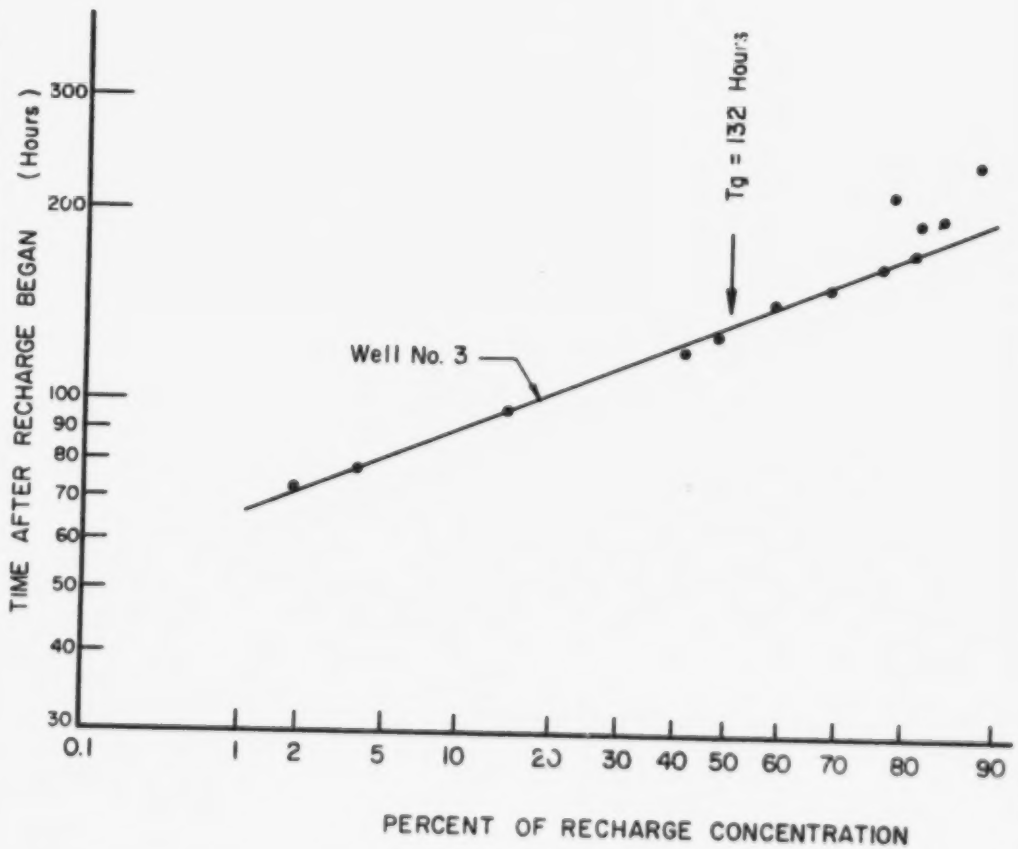
FIGURE V-2



FATE OF DDT AND NITRATE IN GROUND WATER

DETERMINATION OF DETENTION TIME

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FIGURE V-3

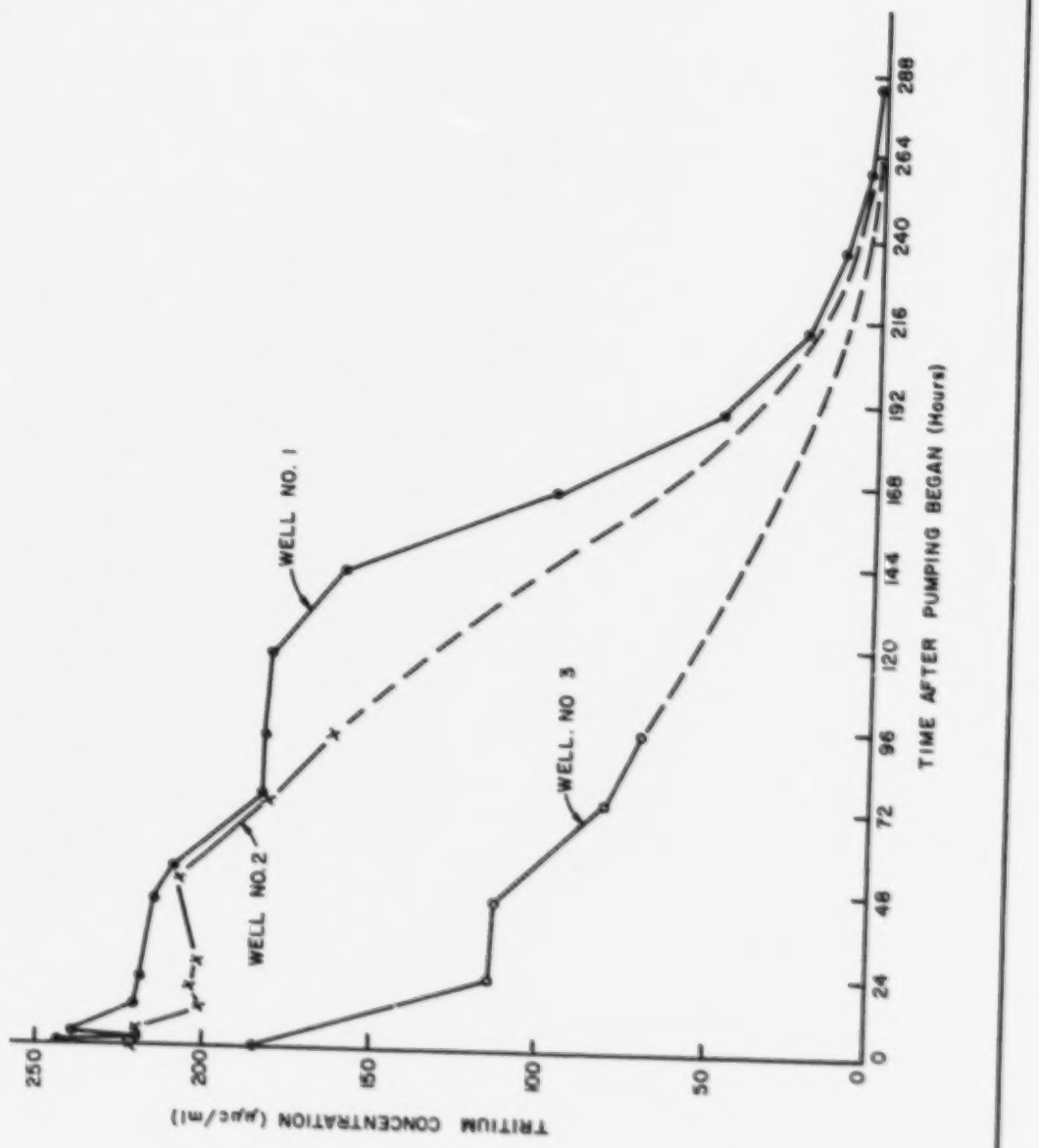
Detention times at the recharge rate of 348 gpm were 1.7 and 5.4 days to Wells No. 2 and 3, respectively. Using the saturated volume calculated from observed water levels, a storage coefficient of 0.23 was calculated.

Following the 10-day recharge period, pumping the recharge well at 504 gpm for 10 days yielded 3.75 curies or 94 percent of the injected tritiated water. Tracer recovery during pumping is shown in Figure V-4. If no losses occurred due to adsorption, breakdown, denitrification, etc., then a similar recovery could be expected for nitrates and DDT. This high recovery of tracer adds to the reliability of tritium as a tracer for determining flow and dispersion characteristics of underground formations.

The recharge well was pumped for 12 days with samples taken each day from Well No. 1. The observation wells were sampled for the first four days and again on the eleventh day when tracer concentrations in all wells had returned to background.

Nitrate Recovery

Nitrate was added to recharge waters with a weighted average concentration of 24.46 mg/l as shown in Figure V-5. Over the 10-day recharge period, this addition amounts to 1,028 pounds of NO_3. The background NO_3 concentration of the supply well was 7.74 mg/l which accounted for 325 pounds in the recharge water, leaving 703 pounds artificially added.



FATE OF DDT AND NITRATE IN GROUND WATER

TRACER RECOVERY WHILE PUMPING WELL NO. 1

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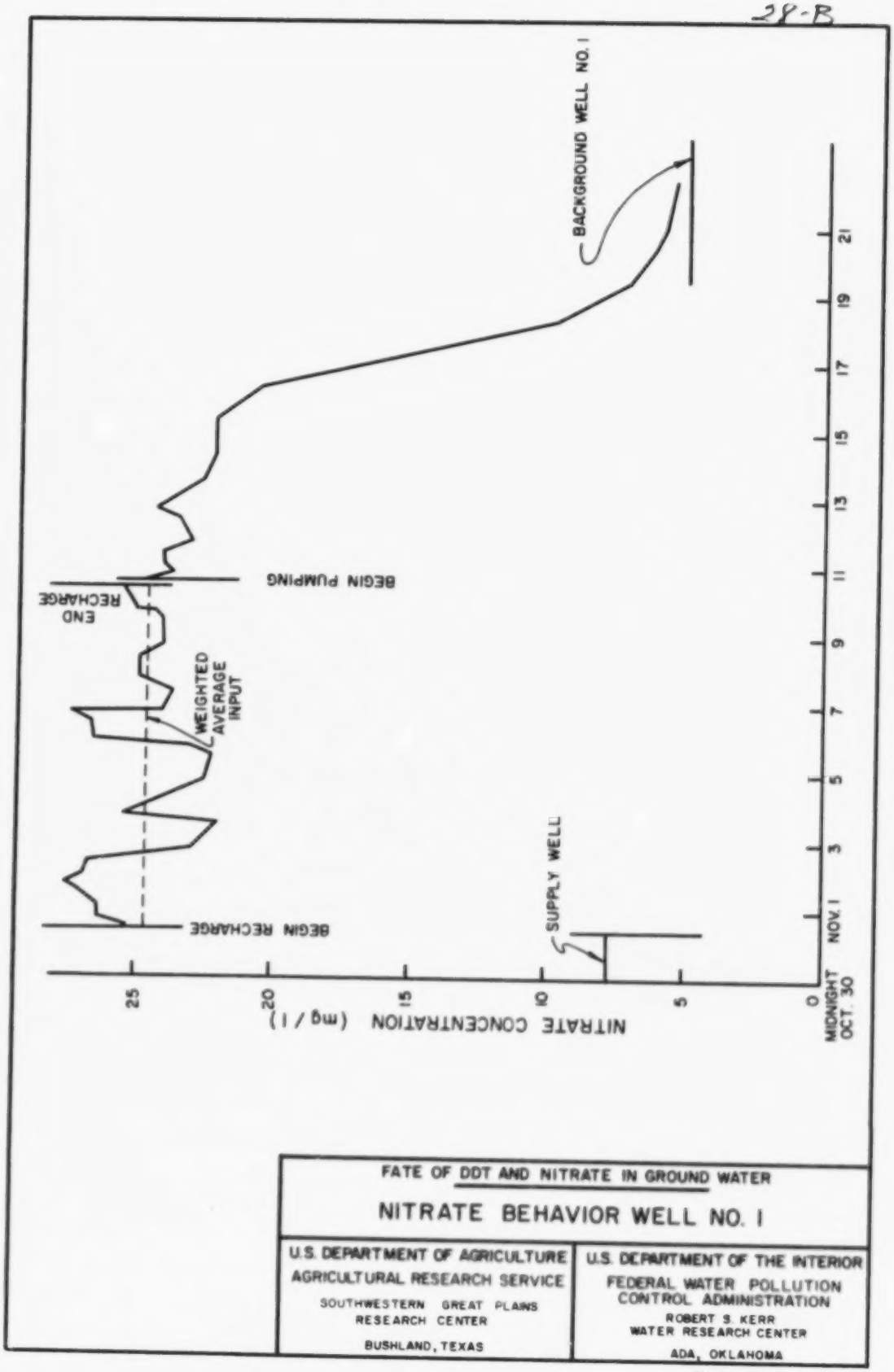
FIGURE V- 4



FATE OF DDT AND NITRATE IN GROUND WATER

NITRATE BEHAVIOR WELL NO. 1

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FIGURE V-5

Figure V-5 also depicts the rate at which NO_3 concentrations were reduced after pumping began. The area under the curve during pumping operations can be equated to pounds of NO_3 produced.

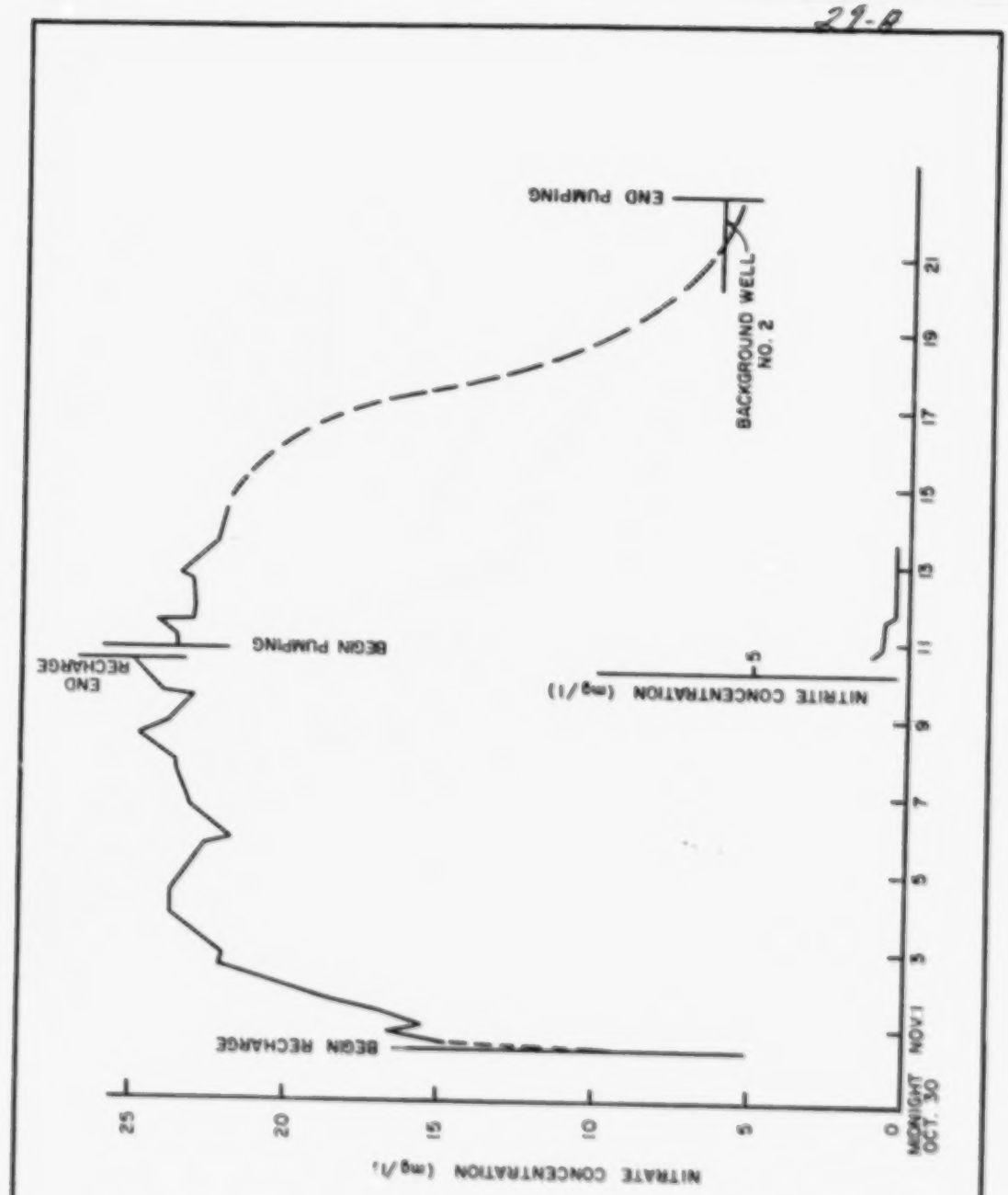
The background of Well No. 1 was 5.00 mg/l which amounts to 360 pounds of the recovered NO_3, leaving 660 pounds recovered of that which was artificially added. This amounts to a nitrate recovery of 94 percent.

Figures V-6 and V-7 show the behavior of nitrates at Wells No. 2 and 3, both under recharge and pumping conditions. As shown, the nitrates in these wells were reduced to near background by the end of the pumping period.

By recovering 94 percent of the nitrate artificially injected, it is apparent that no significant losses were encountered during the test. Although minor concentrations of nitrite (NO_2) were measured at Well No. 2 after pumping began, there was no evidence of extensive denitrification.

Although a high percentage of NO_3 was recovered, it is important to compare its movement with that of the tritiated water. Figure V-8 shows how both the tritium and NO_3 concentrations were evidenced at Wells No. 2 and 3. It is evident that although no significant denitrification occurs, care must be taken in using nitrate as a tracer in ground-water studies.

From Figure V-8, it appears that the nitrates may move somewhat faster than tritium through the aquifer. Undoubtedly, most of the



FATE OF DDT AND NITRATE IN GROUND WATER

NITRATE BEHAVIOR WELL NO. 2

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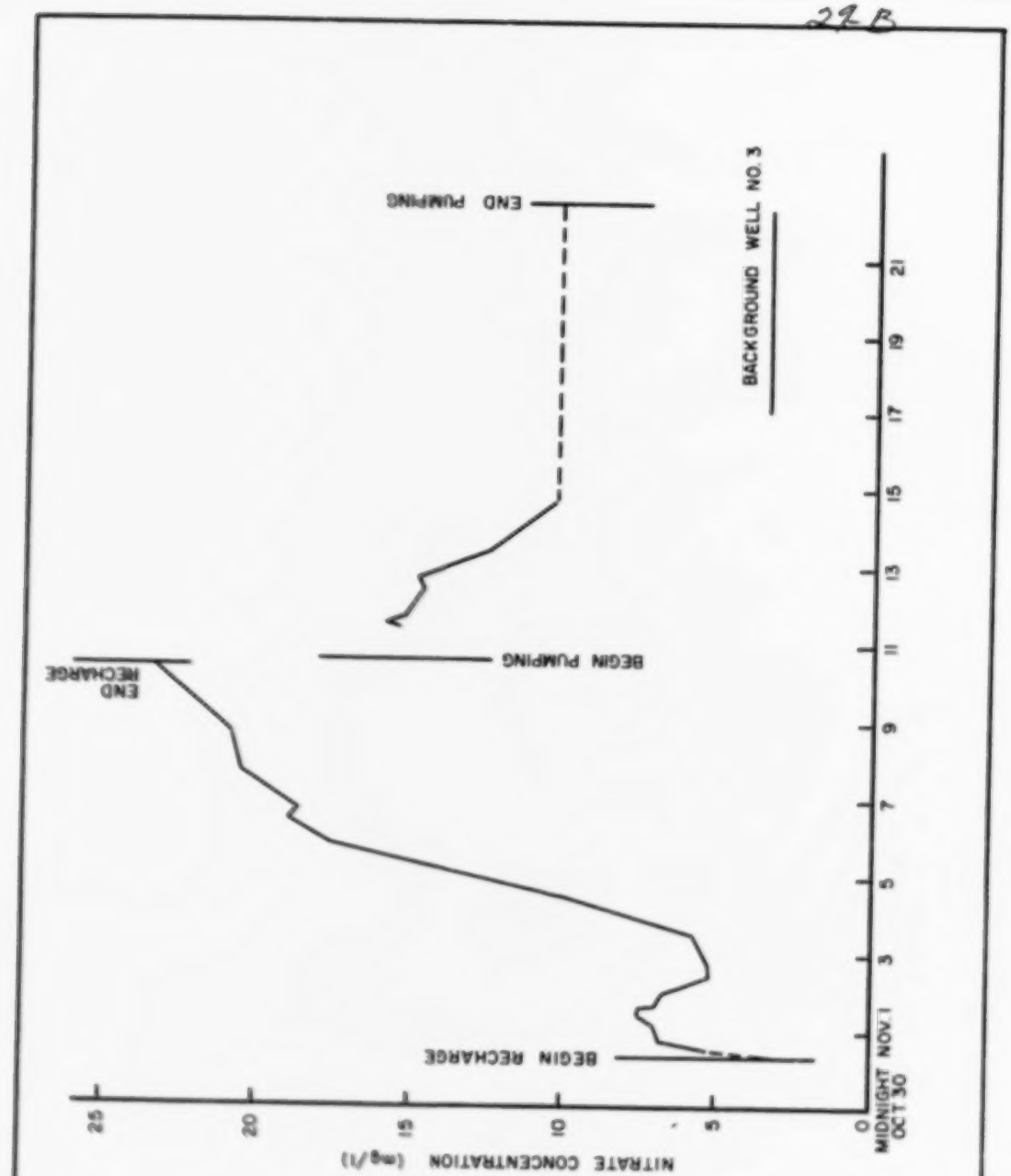
FIGURE V-6



FATE OF DDT AND NITRATE IN GROUND WATER

NITRATE BEHAVIOR WELL NO. 3

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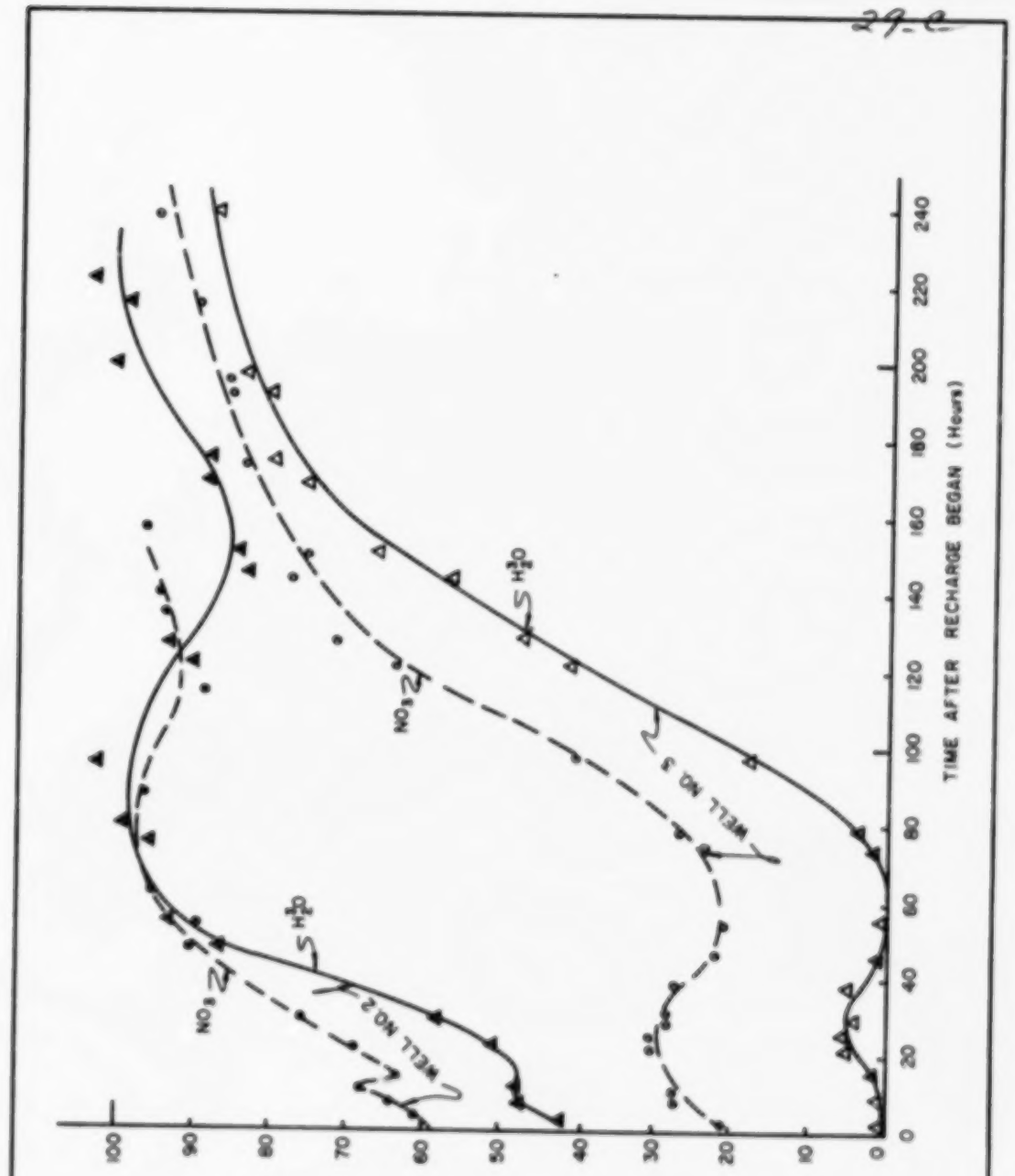
FIGURE V-7



FATE OF DDT AND NITRATE IN GROUND WATER

COMPARISION OF NITRATE AND TRITIATED WATER TRANSPORT

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FIGURE V - 8

difference between the two curves is due to the higher relative background of NO_3 in the recharge area. However, Kaufman and Orlob[27] noted that the chloride ion passed through a natural soil medium faster than tritium and the difference was correlated to clay content of the soil. It was believed that tritiated water molecules passed through the free pore water as did the chloride ion, but the tritiated water also exchanged with the water adsorbed on the clay minerals and with the water of hydration in cations associated with these minerals. Therefore, tritium-labeled water and unlabeled water would be expected to displace almost all of the water in the aquifer. Nitrates could be expected to react in a similar manner to chloride. The clay content of the formation studied at Bushland was low; and, if the effect of background was removed, NO_3 and tritium dispersion curves would be more similar.

A comparison of the use of such tracers can be gained, as an example, in the determination of the aquifer storage coefficient.[28]

Using the nitrate dispersion curves, detention or displacement times between the recharge well and Wells No. 2 and 3 were determined to be 1.3 and 4.4 days, respectively. These detention times with a recharge rate of 348 gpm and a saturated volume calculated from observed water levels yield a storage coefficient of 0.20. This value corresponds to a value of 0.23 obtained by using tritiated water as the tracer.

As shown in Figure V-7, a peak was reached in both NO_3 and tritium concentrations shortly after recharge began. This peak

indicates that some portion of the recharged water moved more rapidly to the observation wells than did other portions. These differences in rates of movement appear to be related to differences in horizontal permeability of the layers comprising the formation.

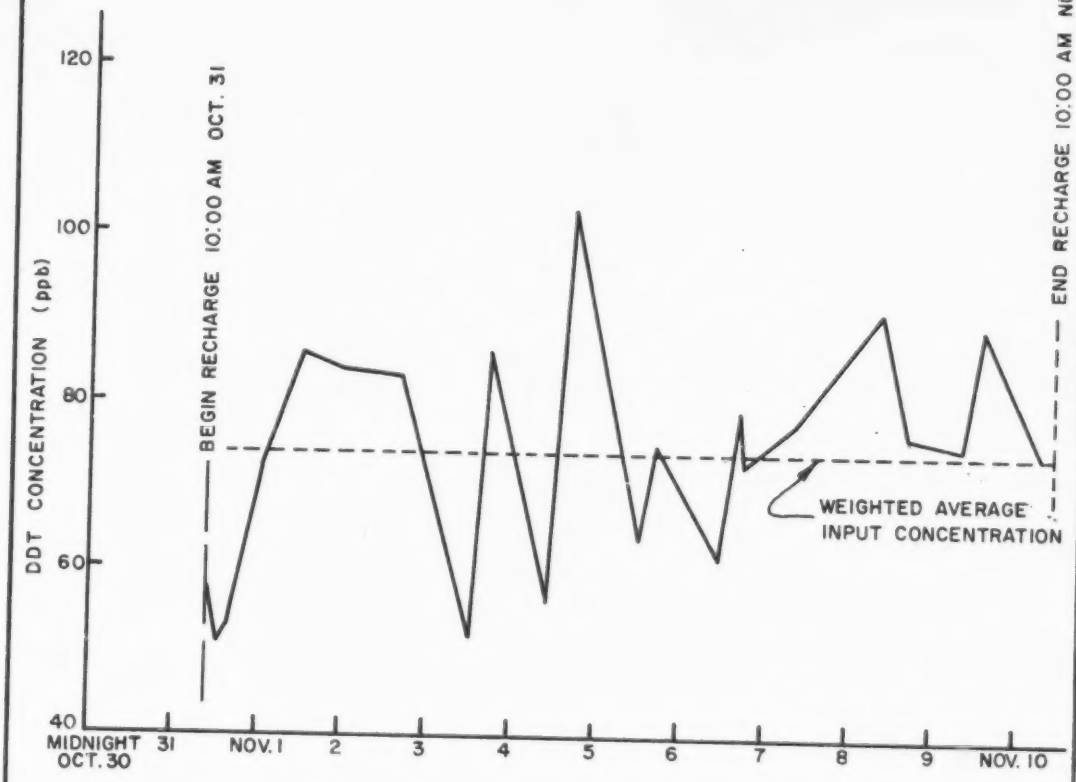
Examination of well logs and laboratory analyses of formation cores revealed that a stratum only a few feet in thickness and lying immediately above the static water table (water level in the wells before recharging began) is considerably more permeable than other strata that transmitted water during the recharge test. For this reason, it is postulated that recharged water moving in this stratum reached the observation wells before any other recharged water; however, as the test proceeded, water from underlying strata entered this stratum as water pressures equalized throughout the saturated part of the formation. Mixing of water from the underlying strata with the recharged water in the layer of higher horizontal permeability resulted in a reduction in concentrations of nitrate and tritium since waters from the underlying strata were at this time largely of native, unaltered quality. This concentration reduction is reflected in curves shown in Figure V-8.

As recharged water began reaching the observation wells from the other strata, concentrations of nitrate and tritium began to gradually increase and the curves took on a shape that would be expected for a situation involving an aquifer having fairly uniform horizontal permeability.

DDT Recovery

Project plans called for the addition of DDT during recharge at a rate of 100 ppb (parts per billion) or 100,000 ng/l (1 nanogram = 10^{-9} grams). Difficulties in controlling the chemical feed rate reduced this to about 90 ppb total DDT, or 74 ppb p,p'-DDT, the principal DDT isomer which was routinely determined in this work. With a recharge rate of 348 gpm, the actual input of p,p'-DDT amounted to 3.11 pounds during the 10-day recharge period. The input concentration of p,p'-DDT, as measured in the recharge stream, is shown in Figure V-9.

Analyses of water samples from Well No. 2, 33 feet from the recharge well, indicates a probable slight increase in DDT in this well during the recharge period. However, the concentration of about 0.4 ppb DDT in water from this well after 10 days of recharge was much more comparable with the background concentration of 0.1 ppb DDT at the beginning of recharge than with the concentration of 74 ppb DDT in the recharge water, and it would appear that no significant breakthrough of DDT to Well No. 2 occurred during the period of this study. No increase in DDT in Wells No. 3 and 4, 66 and 150 feet respectively from the recharge well, was noted during the recharge period. The DDT entering the aquifer with the recharge water must, therefore, have been largely adsorbed onto the aquifer material near the recharge well.



FATE OF DDT AND NITRATE IN GROUND WATER

DDT RECHARGE CONCENTRATION

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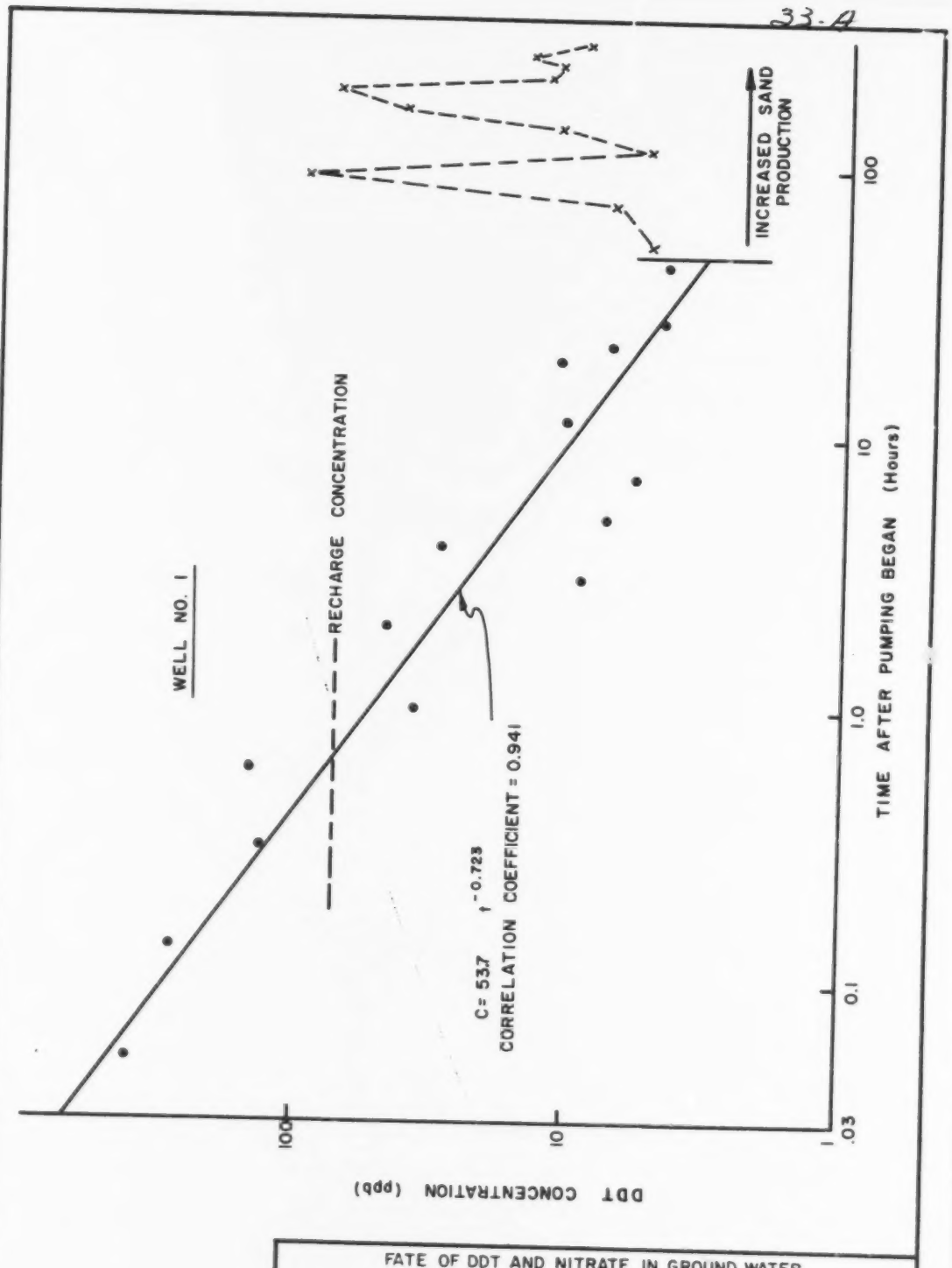
FIGURE V-9

Recharge ended at 10:00 a.m., November 10, 1967; and, after three hours of inactivity, pumping of the recharge well began at 1:00 p.m. The pumped stream was sampled in order to determine: (1) the amount of DDT in the water, both in solution and suspension; (2) the DDT adsorbed per gram of produced sand; and (3) the amount of sand produced on a temporal basis. (The term DDT as employed herein refers to p,p'-DDT only.)

Figures V-10 and V-11 show the concentration of DDT in the pumped water. (Figure V-11 uses arithmetic scales and provides a better picture of the relative times involved.) Although the well was recharged with 74 ppb DDT, the first sample--collected one minute after pumping began--showed a DDT concentration of 1,204 ppb. Hence, the initial concentration of produced water was over 16 times that of the recharge water. On the basis of reported studies of the solubility of DDT in water,[29,30,31,32] it is evident that much of this DDT was not in true solution, but probably occurred as minute, undissolved particles in suspension or was adsorbed to colloidal soil particles suspended in the water.

Although the initial DDT concentration of the pumped water was very high, it decreased rapidly during the early period of pumping and was reduced by two orders of magnitude after only 10 hours of pumping at 504 gpm.

There are two significant portions of the DDT recovery curve shown in Figures V-10 and V-11. Throughout the first two days of



FATE OF DDT AND NITRATE IN GROUND WATER

DDT CONCENTRATION AFTER PUMPING BEGINS

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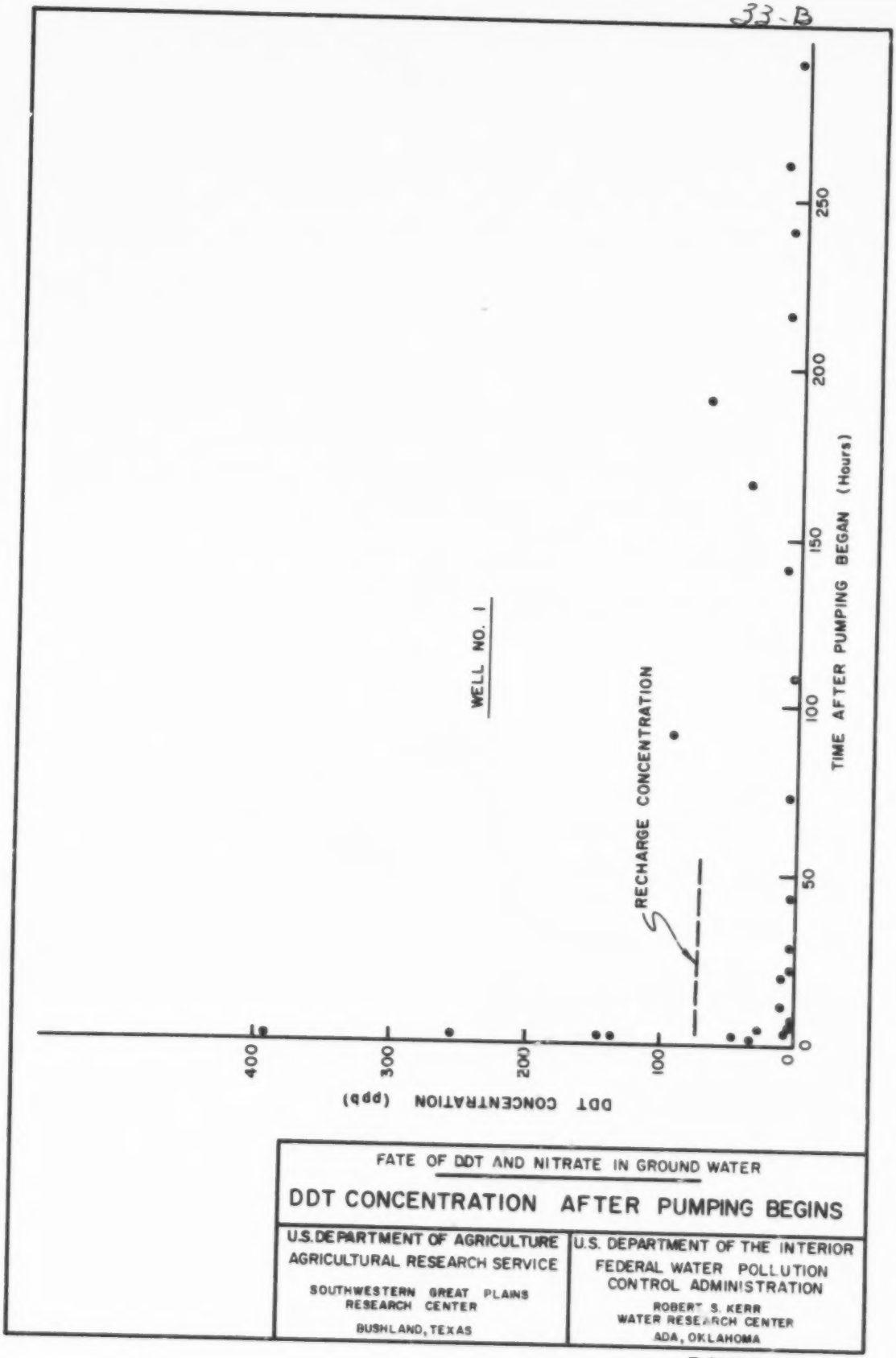
FIGURE V-10



FATE OF DDT AND NITRATE IN GROUND WATER

DDT CONCENTRATION AFTER PUMPING BEGINS

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FIGURE V-11

pumping the measured DDT concentration continued to decrease at decreasing rate with time, following the relationship shown in Equation V-1 with a correlation coefficient of 0.941.

$$C = 53.7\ t^{-0.723} \qquad \text{Eq. V-1.}$$

where C = concentration of DDT in produced water (ppb)

t = time after pumping began (hours)

Hence, after pumping for 27.5 hours, the DDT concentration of the produced water had declined to 4.8 ppb by actual measurement and to a calculated value of 4.9 ppb by Equation V-1; similarly determined and calculated values after 43.5 hours were 4.6 and 3.5 ppb, respectively. During the third day of pumping, however, determined DDT concentrations of pumped water began to differ significantly from values calculated by means of Equation V-1. For the remainder of the pumping period DDT concentrations considerably exceeded those predicted by Equation V-1 and were often quite erratic. On three occasions--the fourth, seventh, and eighth days--measured DDT concentrations were relatively high, approaching or exceeding the recharge concentration. That rapid fluctuation of DDT concentration of produced water may have been occurring during this period was indicated by an almost twofold difference (121.0 and 67.7 ppb) in DDT concentrations of samples collected in immediate succession on the fourth day of pumping. Unfortunately, samples were not collected with sufficient frequency after the fourth day to permit confirmation of this apparent phenomenon.

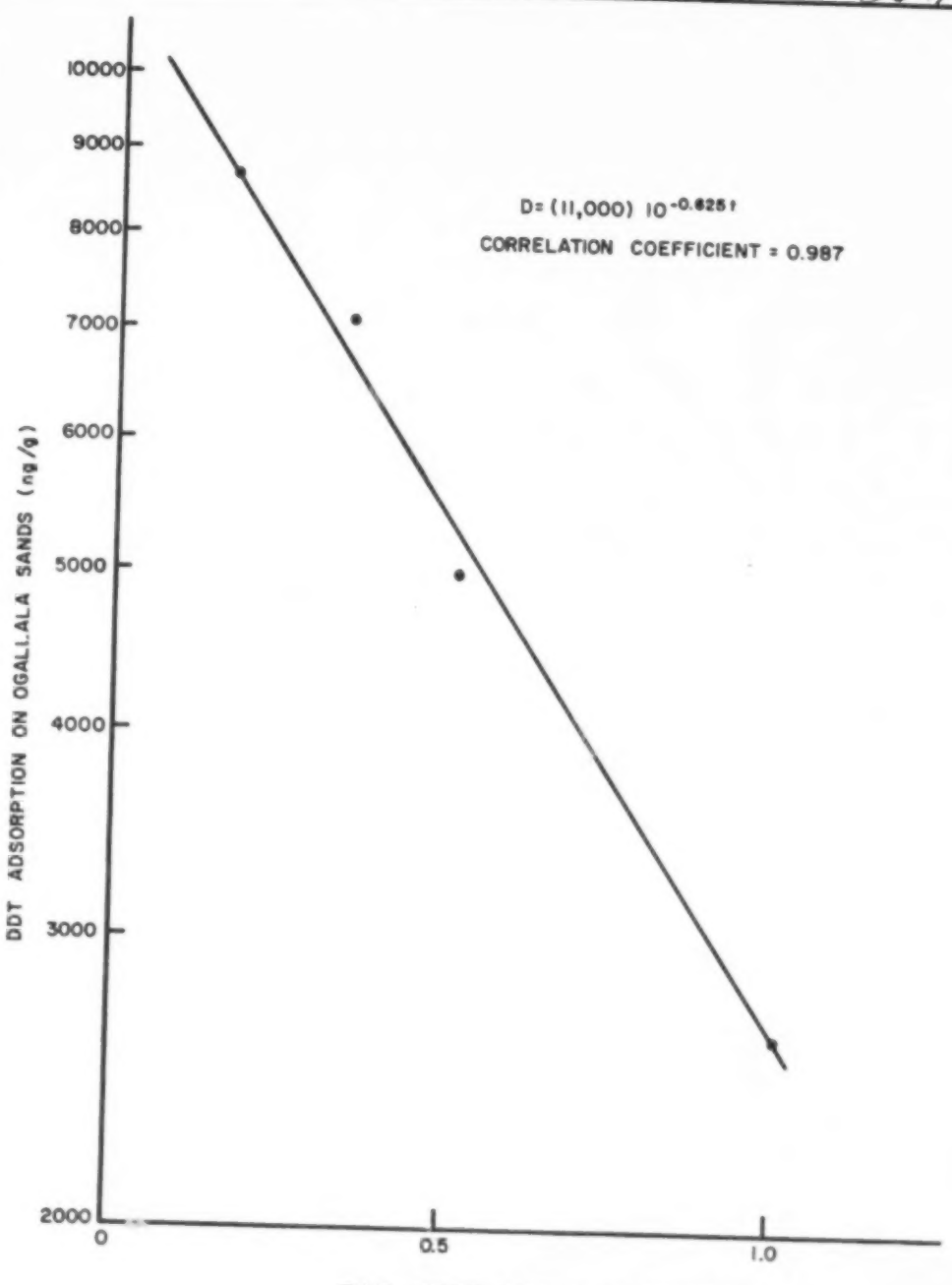
The observed recovery of DDT in produced water becomes more understandable if concurrent production of sand during pumping of the well is considered. For the first two days, when DDT concentrations were declining regularly, sand produced by pumping the well was decreasing or relatively constant at a low level, following an initial heavy production during the first two or three hours of pumping. During the third and fourth days of pumping, however, when DDT concentrations became erratic and higher than expected, there was a sudden and sporadic increase in sand production; and for the remainder of the pumping period sand production gradually increased, although never attaining a very high level relative to production during the early hours of pumping. This increased sand production almost certainly indicated major disturbances, possibly cave-ins, in the aquifer material near the well casing. Such disturbances would be likely to expose fresh surfaces of particulate matter which constitutes the aquifer. Water flowing at high velocity over these newly exposed surfaces might result in more rapid removal of adsorbed DDT and higher DDT concentrations in produced water. Also, such disturbances would likely result in increased and nonuniform release of colloidal soil particles high in adsorbed DDT, as well as colloidal particles of DDT which might be lodged in the interstitial areas of the aquifer material. Although all samples were screened during collection, as previously described, such colloidal particles would

not be removed and would greatly increase DDT content of samples receiving them. It is quite plausible, therefore, that the increased and variable DDT concentrations of samples of water produced after the second day of pumping were manifestations of disturbances in aquifer structure.

Integration of Equation V-1 from 0 to 48 hours, the period during which DDT content of produced water was decreasing regularly with time, indicates that only 0.142 pound of DDT was recovered in produced water during the first two days of pumping the recharge well. Quantitative estimation of DDT recovered in produced water during the remaining ten days of pumping cannot be made, however, because of the indicated variability of DDT concentration in pumped water and the relative infrequency of sampling during this period.

Another means by which DDT can be removed from the formation after a recharge operation is by the production of sand in the pumped stream. Analysis of produced sand in this study indicated a considerable capacity of the Ogallala sand for adsorption of DDT; this is consistent with a recent report of relatively high adsorption of DDT from aqueous medium onto fine sand in laboratory studies.(33)

During the early hours of pumping, the amount of DDT adsorbed per unit weight of produced sand was found to decrease regularly with time as shown in Figure V-12 and according to Equation V-2 with a correlation coefficient of 0.987



FATE OF DDT AND NITRATE IN GROUND WATER

ANALYSIS OF DDT ADSORPTION ON OGALLALA SAND

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FIGURE V-12

$$D = (11{,}000)\ 10^{-0.625t} \qquad \text{Eq. V-2.}$$

where D = DDT adsorbed per gram of sand (ng/g)

t = time after pumping began (hours)

The amount of sand recovered during early phases of pumping is shown on a temporal basis in Figure V-13. These data can be formulated as shown by Equation V-3 with a correlation coefficient of 0.956.

$$W = (268{,}500)\ 10^{-1.611t} \qquad \text{Eq. V-3}$$

where W = rate of produced sand (grams/hour)

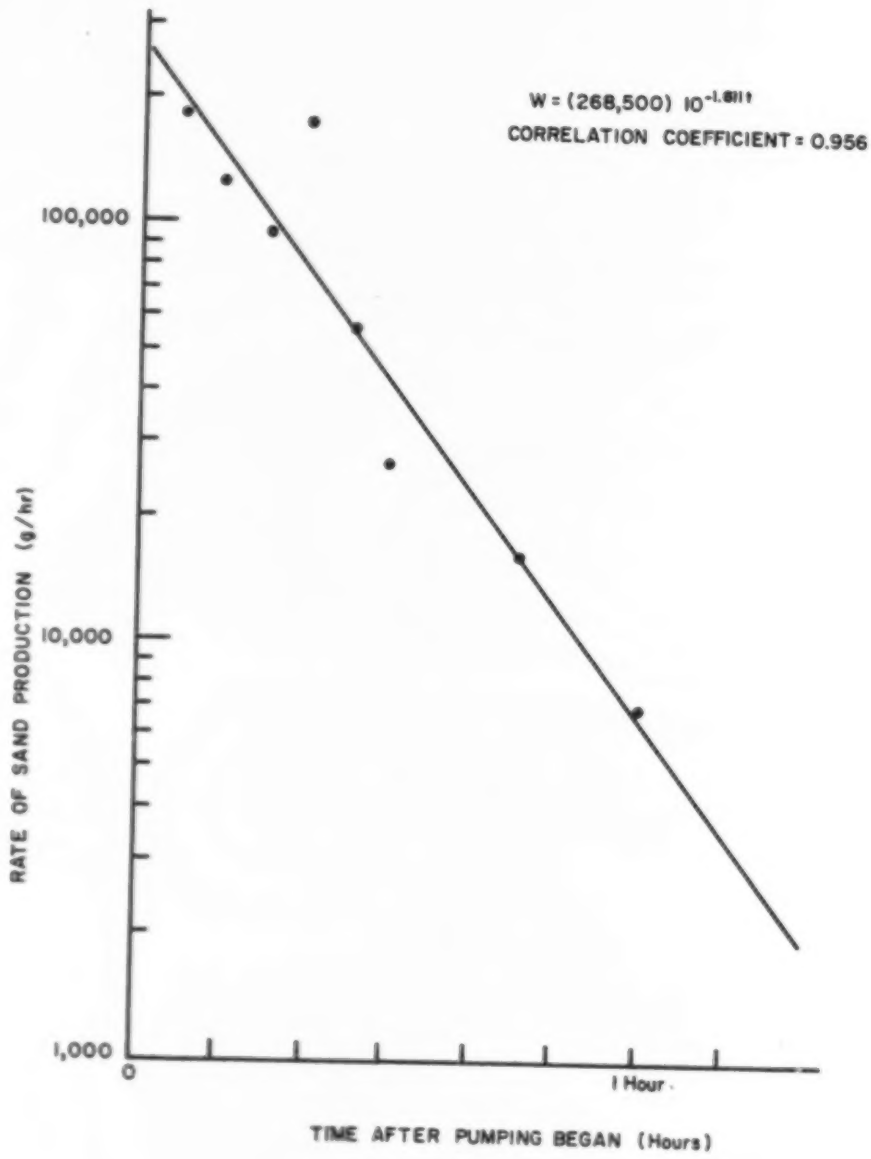
t = time after pumping began (hours)

By integrating Equations V-2 and V-3 the quantity of DDT recovered on produced sand during the early phases of pumping can be calculated. Because of rapid decrease with time of sand produced and DDT adsorbed per unit weight of sand, the rate of DDT recovery on sand was most rapid during the first few minutes after pumping began as shown in Table V-1.

Table V-1

Rate of DDT Recovery on Sand
After Pumping Began

Time After Pumping Began (Minutes)	Total Weight of DDT Recovered (Grams)
5	0.20
10	0.33
15	0.40
20	0.45
25	0.51
30	0.53
35	0.54
40	0.55
45	0.56
60	0.57



FATE OF DDT AND NITRATE IN GROUND WATER

RATE OF SAND PRODUCTION AFTER PUMPING BEGINS

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FIGURE V-13

Hence, almost all of the adsorbed DDT which was recovered by sand production during the first two days of pumping was recovered within the first hour after pumping began. It appears that most of the sand which contributed significantly to DDT recovery during this period was probably either in the well casing when pumping began or moved from the aquifer very quickly.

As previously noted, sand production sporadically increased during the third and fourth days of pumping and gradually increased thereafter until the end of this investigation. It seems unlikely that significant DDT was recovered adsorbed to produced sand during this period, however, because the magnitude of sand production was not sufficient to contribute much DDT at observed levels of adsorption.

It should be noted that the sand collected for DDT adsorption characteristics in this study did not reflect all of the fines because of sampling procedure. Since the fine particles, particularly those high in clay, present with the aquifer solids are likely to adsorb significant quantities of DDT, the indicated recoveries of DDT adsorbed on sand in this investigation may be low. Nevertheless, it appears a valid conclusion that the quantity of DDT recovered by production of sand in this study was probably small compared with the amount recovered in produced water.

Summation of the DDT recovered in the produced water and adsorbed on the produced sand during the first two days of pumping indicates that less than 5% of the total system input was recovered during this period of pumping the recharge well.

Although the data obtained in this study are not sufficient to permit quantitative estimation of DDT recovered during the full 12-day pumping period, they do indicate that a major proportion of the DDT introduced into the aquifer during recharge remained adsorbed in the aquifer following termination of pumping.

VI. SUMMARY AND CONCLUSIONS

This project was a cooperative venture between the Robert S. Kerr Water Research Center of the U. S. Department of the Interior and the Southwestern Great Plains Research Center of the U. S. Department of Agriculture. The work was done at Bushland, Texas.

The Ogallala Aquifer was recharged at 348 gpm for a period of 10 days with water taken from an irrigation well 2,280 feet from the recharge point.

Tritiated water, nitrate, and p,p'-DDT were injected into the recharge stream at concentrations of 210 μμc/ml, 24.46 mg/l, and 74 ppb, respectively.

The system was monitored by chemical analyses of samples taken at several observation wells with principal interest in those located at 33, 66, and 150 feet from the injection well. Water levels were monitored continuously at 16 points located up to 1,000 feet from the recharge well.

At the end of the recharge period, the system was allowed to stabilize for three hours before pumping began at a rate of 504 gpm. The well was pumped at that rate for 12 days with the system continuing to be monitored for chemical and hydraulic parameters.

Tritiated water (H^3_2O) can be used satisfactorily in groundwater studies to define the movement of water and at the same time

describe the aquifer's characteristics such as storage coefficient. This is evidenced by its physical and chemical characteristics and a demonstrated recovery of 94 percent. At the end of the 12-day pumping period, the tritiated water had been removed from the aquifer.

With a recovery of 94 percent, there was not evidence of nitrate loss due to denitrification; however, the behavioral pattern at the observation wells was not the same as that of the tritiated water. This was due mainly to the difficulties in accountability to the aquifer's nitrate background. After the end of pumping, the aquifer had returned to near its original nitrate background.

There was no significant breakthrough of DDT to the first observation well 33 feet from the recharge well. Apparently, the injected DDT was largely adsorbed to the aquifer material near the recharge-pumping well.

The DDT concentration in the pumped water was over 16 times the recharge concentration at initiation of pumping but decreased to below the recharge concentration in about one hour and continued to decrease at a decreasing rate during the first two days of pumping. DDT concentrations then became erratic and on three occasions approached or slightly exceeded recharge concentration, apparently as a result of disturbances in the aquifer structure.

The amount of DDT recovered adsorbed on sand was relatively small, but a considerable capacity of Ogallala Aquifer material for adsorption of DDT was shown.

Apparently, a major proportion of the DDT introduced into the aquifer during recharge was not recovered during pumping but remained in the aquifer.

The three most important points resulting from this study are:

1. When present, nitrate pollution of the Ogallala is probably of more immediate concern than DDT because of its ability to move through the aquifer.
2. A well, used for domestic purposes, should not be recharged with water in which DDT is suspected because of the possible release of DDT contaminated aquifer material into water subsequently pumped from the well.
3. Considerable caution must be used in extending this work to other pesticides because of the myriad of solubilities and the obviously varied adsorption characteristics encountered.

VIII. BIBLIOGRAPHY

1. Bailey, George W. and White, Joe L., "Review of Adsorption and Desorption of Organic Pesticides by Soil Colloids, with Implications Concerning Pesticide Bioactivity." Agricultural and Food Chemistry 21:324-332. July-August 1964.

2. Pesticides and Their Effects on Soils and Water. ASA Special Publication No. 8. Madison, Soil Science Society of America, Inc., November 1966. 127 p.

3. Bailey, George W. and White, Joe L., "Adsorption of Organic Herbicides by Montmorillionite: Role of pH and Chemical Character of Adsorbate." Presented at American Society of Agronomy National Meeting, Columbus, Ohio, November 1, 1965. 13 p.

4. Nash, Ralph G. and Woolson, Edwin A., "Persistence of Chlorinated Hydrocarbon Insecticides in Soils." Science, 157: 924-927.

5. Knutson, Herbert, "Relationships Between Pesticidal Application and Water Contamination Under Irrigation in the Great Plains." Grant Proposal from Department of Entomology of Kansas State University, March 1966. 12 p.

6. Smith, George E., "Nitrate Problems in Plants and Water Supplies in Missouri." Presented at Second Annual Symposium on the Relation of Geology and Trace Elements to Nutrition, 92nd Annual Meeting American Public Health Association, New York City, October 7, 1964. 21 p., 9 tables, 8 figures. (Missouri Agricultural Experiment Station Journal Series No. 2830)

7. Larson, T. E. and Henley, Laurel, "Occurrence of Nitrate in Well Waters." University of Illinois Water Resources Center, Final Report Project 65-05G, June 1966. 8 p., 5 tables, 2 figures.

8. Hanway, J. J., et al, "The Nitrate Problem." Iowa State University of Science and Technology Special Report No. 34, August 1963. 20 p.

9. Keller, W. D. and Smith, George E., "Ground-Water Contamination by Dissolved Nitrate." Presented at 1964 Meeting of Geological Society of America, Miami, Florida. 27 p.

10. Case, A. A., et al, "Nature and History of the Nitrate Problem." Science and Technology Guide, August 1964. 2 p.

11. Lenain, August F., "The Impact of Nitrates on Water Use." Jour. AWWA, August 1967. p. 1049-1054.

12. Smith, George E., "Nitrate Problems in Plants and Water Supplies in Missouri." Presented at Second Annual Symposium on the Relation of Geology and Trace Elements to Nutrition, 92nd Annual Meeting American Public Health Association, New York City, October 7, 1964. 21 p., 9 tables, 8 figures. (Missouri Agricultural Experiment Station Journal Series No. 2830)

13. Allison, Franklin E., "The Fate of Nitrogen Applies to Soils." Advances in Agronomy 18:219-258. 1966.

14. Stewart, et al, "Nitrate Pollution under Feed Lots and Agricultural Lands." Agricultural Research Service, U. S. Department of Agriculture, ARS 41-134. 1967.

15. White, A. W., Barnett, A. P. and Jackson, W. A., "Nitrogen Fertilizer Loss in Runoff." Crops and Soils 19:4. January 1967.

16. Rayner, Frank A., "The Ground-Water Supplies of the Southern High Plains of Texas." Proceedings of the Third West Texas Water Conference, February 5, 1965. pp. 20-42.

17. Hauser, V. L., and Lotspeich, F. B., "Artificial Ground-Water Recharge Through Wells." J. Soil and Water Conserv. 22:1. 1967.

18. Rebhum, M. and Hauser, V. L., "Clarification of Turbid Water with Polyelectrolytes for Recharge Through Wells." Proceedings Symposium on Artificial Recharge and Management of Aquifers, Haifa, International Association for Science Hydrology, Publication No. 72, pp. 218-228. 1967.

19. Jacob, C. E., "Drawdown Test to Determine Effective Radius of Artesian Well." Trans. ASCE 112:1047-1070. 1947.

20. Texas Board of Water Engineers, "Artificial-Recharge Experiments at McDonald Well Field, Amarillo, Texas." Bulletin 5701, 34 p. January 1957.

21. McMillion, Leslie G. and Keeley, Jack W., "Sampling Equipment for Ground-Water Investigations." Ground Water Research Program, Robert S. Kerr Water Research Center, Ada, Oklahoma, December 1967. 3 p., 2 figures.

22. Technicon Corporation, Ardsley, New York.

23. Kamphake, L. J., Hannah, S. A., and Cohen, J. M., "Automated Analysis for Nitrate by Hydrazine Reduction." USDI, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

24. Breidenbach, A. W., et al, "The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters." USDI, FWPCA, WP-22, November 1966. 70 p.

25. Hagen, R. E., et al, "A Chromatographic-Fluorometric Method for Determination of Naringin, Naringenin Rutinoside, and Related Flaranone Glycosides in Grapefruit Juice and Juice Sacs." Analytical Biochemistry 12:472. 1965.

26. U. S. Geological Survey, Double Mass Curves, Manual of Hydrology: Part 1 General Surface Water Techniques. Washington, U. S. Government Printing Office. 1960. (Geological Survey Water Supply Paper 1541-B)

27. Kaufman, W. J. and Orlob, G. T., "Measuring Ground-Water Movement with Radioactive and Chemical Tracers." Jour. AWWA 48(5). May 1956.

28. Slichter, Charles S., Theoretical Investigation of the Motion of Ground Waters. Ground Water Notes Hydraulics No. 22. June 1954. 80 p.

29. Babers, F. H., J. Am. Chem. Soc. 77:466. 1955.

30. Richards, A. G., and Cittkomp, L. K., Biol. Bull. 90:97. 1946.

31. Roeder, K. D., and Weiant, E. A., "The Site of Action of DDT in the Cockroach." Science 103:304. 1949.

32. Bowman, M. C., Acree, F. Jr., and Corbett, M. K., "Solubility of Carbon-14 DDT in Water." Agricultural and Food Chemistry 8:406. 1960.

33. Hill, D. W. and McCarty, P. L., "Anaerobic Degradation of Selected Chlorinated Hydrocarbon Pesticides." Journal Water Pollution Control Federation 39 :1259. 1967.